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Reactions of Thianthrene Cation Radical Perchlorate with Azo-bis-2-phenoxy-2-propane and Azo-bis-2-(p-nitrophenoxy)-2-propane

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Thianthrene cation radical perchlorate (1) reacted with azo-bis-2-phenoxy-2-propane (6) to give thianthrene (2), *cis*-thianthrene-5,10-dioxide, 5-(p-hydroxyphenyl) thianthrenium perchlorate (10), acetone, phenol, and 5-(2-propenyl) thianthrenium perchlorate (11) when the mole ratio of 1 to 6 was 1:1. Among the products, 11 was a new compound. However, when the corresponding mole ratio was 5:1, 11 was not formed. Similar result was obtained for azo-bis-2-(p-nitrophenoxy)-2-propane.

Introduction

Some years ago we have investigated the reaction of thianthrene cation radical perchlorate (1) with azobisisobutyronitrile (AIBN) in acetonitrile at solvent reflux temperature in order to obtain information about the coupling nature between a cation radical and a free radical.[1] From this reaction were obtained thianthrene (2), thianthrene 5-oxide (3), *cis*-thianthrene-5,10-dioxide (4), 5-acetonylthianthrenium perchlorate (5), and 5-(2-thianthreniumyl) thianthrene perchlorate. No coupling product between 1 and cyanoisopropyl radical was detected. In addition, it was realized that a canonical form of cyanoisopropyl radical caused the reaction complicated. Therefore, it was necessary to change CN group of AIBN with other group of which resonance form would not be expected to involve either in the reaction with 1 or in the cross-coupling reaction of the radical itself. We synthesized azo-bis-2-(phenoxy)-2-propane (6) according to the known method[2] and run the reaction with 1. Surprisingly, the azo compound (6) underwent rapidly the reaction with 1 in acetonitrile at room temperature. We wish to report the result in this paper.

Experimental

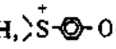
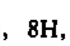
Thianthrene (2) and thianthrene cation radical perchlorate (1) were prepared by the methods described elsewhere.[3] Acetonitrile was Kanto Chemical Corporation Extra pure and was refluxed with phosphorus pentoxide for 3 hours, followed by refluxing with calcium hydride for 2 hours. The distillate was stored over molecular sieve (4Å). Hydrazine hydrate (80%) was from Kanto. Column chromatography was performed with Merck silica gel (70-230 ASTM mesh, 0.063-0.2mm). All chromatographic solvents were distilled prior to use. Ultraviolet spectra were obtained with a Beckman 5270 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 283 infrared spectrometer. All infrared spectra were taken using potassium bromide pellets, unless otherwise indicated. ^{1}H NMR spectra were recorded on a Varian EM-360A spectrometer and chemical shifts were relative to tetramethylsilane. Melting points were measured using a Fisher-Jones melting point apparatus and uncorrected.

Preparation of methyl methylketazine (7). The compound was prepared by the reaction of acetone with 80% hydrazine hydrate in ether according to the known procedure.[4]

Preparation of azo-bis-2-chloro-2-propane (8). The title compound was prepared by bubbling of chlorine gas into 7 in petroleum ether at 0°C. The reaction mixture was worked up as in the literature.[2] Chlorine gas was generated by the reaction of $KMnO_4$ with conc. HCl which was passed through water, followed by conc. H_2SO_4.

Preparation of azo-bis-2-phenoxy-2-propane (6). To a 180 ml of 75% aq. ethanol containing 5.4g (0.14 mmol) of NaOH was added 15g (0.16 mmol) of phenol. After the solution cooled to room temperature, 12.9g (0.07 mol) of 8 was added little by little by which time yellow precipitates were formed. The reaction mixture was additionally stirred for 30 min, followed by dilution with 160 ml of water. The yellow solid was filtered, washed with water, followed by recrystallization from methanol, yielding 4.2g (20%) of white solid: mp 90-90.5°C (lit.[2] 90-90.5°C); IR (KBr) 1595, 1490 ($-N=N-$)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 12H, CH_3), 6.90-7.20 (m, 10H, C_6H_5).

Preparation of azo-bis-2-(p-nitrophenoxy)-2-propane (9). To a 90 ml of 75% aq. methanol containing 3.5g (0.088 mol) of NaOH was added 12.5g (0.089 mol) of p-nitrophenol. The mixture was stirred at about 40°C to cause a homogeneous solution. To this solution was added little by little 6g (0.033 mol) of 8. The mixture was continuously stirred for 2 hours, followed by dilution with 50 m*l* of water. The precipitate formed was filtered and washed with water. Yield was 0.5g (4%): mp 149.5-150°C (EtOH-MeOH); IR (KBr) 1515, 1495 ($-N=N-$) 1340 ($-NO_2$ stretch)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 12H, CH_3), 7.03, 8.04 (2d, 8H, $C_6H_4NO_2$).

Reaction of 1 *with* 6 *in the air.* To a stirred solution of 1.885g (5.98 mmol) of 1 in 25 m*l* of acetonitrile was added 2.320g (5.98 mmol) of 6. The purple color of the cation radical changed to pale green color. The solution was stirred for 4 hours and then the solvent was removed by a rotary evaporator using a cold trap (−78°C). The residue was chromatographed on a silicagel column (13×2cm). Elution with hexane (480 m*l*) gave 883 mg (4.09 mmol) of 2. Elution next with benzene (75 m*l*) gave 813 mg (8.65 mmol) of phenol which was identified by ^{1}H NMR and IR spectra. Next benzene (150 m*l*) fraction gave 64 mg of a colorless liquid which was solidified in 3 hours in the air. However, it was unsuccessful to obtain pure compound. Elution with ether afforded 55 mg (0.22 mmol) of 4: mp 282-283°C (EtOH) (lit.[5] 283-284°C); IR (KBr) 1080, 1020 (S=O stretch), 750, 530cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6-8.15 (m, aromatic); UV λ_{max}^{MeOH} 210 nm. Elution with ethyl acetate (60 m*l*) gave 211 mg of unknown compounds. Next ethyl acetate fractions (75 m*l*×3) gave 495 mg (1.21 mmol) of 5-(p-hydroxyphenyl)thianthrenium perchlorate (10): mp 256-257°C (lit.[6] 255.5-256.5°C); IR (KBr) 3240, 1582, 1100, 838, 750, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 6.92-7.37 (2d, 4H, ), 7.75-8.54 (m, 8H, ), 10.55 (s, 1H, OH); UV $\lambda_{max}^{CH_3CN}$ 316, 267 nm. Elution with acetone (150 ml) gave 110 mg (0.31 mmol) of a white solid: mp (dec) 166-167°C (CH_3CN-ether); IR (KBr) 3038, 2995, 1572 (C=C stretch), 1090, 620 (ClO_4^-) cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 1.95 (s, 3H, CH_3), 5.15, 6.00 (d, 2H, $=CH_2$), 7.65-8.55 (m, 8H, aromatic); UV $\lambda_{max}^{CH_3CN}$ (log ε) 307 (3.74), 260 (3.68), 222 (4.34) nm. Anal. Calcd for $C_{15}H_{13}S_2ClO_4$: C, 50.49; H, 3.67; S, 17.97; Cl, 9.94. Found: C, 49.66; H, 3.60; S, 17.54; Cl, 10.35. The compound was assigned to be 5-(2-propenyl) thianthrenium perchlorate (11).

Reaction of the trapped solution with 1 *in the air.* The frozen solution at −78°C melted by raising the temperature. To this was added 215 mg (0.68 mmol) of 1, which was stirred for 12 hours by which time the purple color of the cation radical solution became faint. By the addition of small amount of water, the color of the solution turned pale red. After the solvent was removed under vacuo, the residue was chromatographed on a silica gel column. Elution with hexane gave 68 mg (0.31 mmol) of 2. Elution with benzene afforded 42 mg (0.18 mmol) of 3. Elution next with acetone afforded 48 mg (0.12 mmol) of 5, which was identified by the spectroscopic data.[7]

Reaction of 1 *with* 6 *in the air.* To a stirred solution of 2.167 g (6.85 mmol) of 1 in 25 m*l* of acetonitrile was added slowly the azo compound (6) until the purple color of the cation radical had disappeared. The amount of 6 added was 383 mg (1.28 mmol). After the solvent was removed under vacuo, the residue was chromatographed on a silica gel column (12×2cm). Elution with hexane (600 m*l*) gave 732 mg (3.39 mmol) of 2. Elution with benzene (75 m*l*×2) afforded 12 mg (0.048 mmol) of thianthrene-5,5-oxide (12): mp 167-168°C (EtOH) (lit.[5] 168-169°C); IR (KBr) 1320, 1310, 1110 (SO_2 stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40-7.68 (m, 6H), 8.15-8.32 (m, 2H); UV λ_{max}^{MeOH} 226, 261, 282, 318 nm. Elution with ether (75×3 m*l*) gave 40 mg (0.16 mmol) of 4. Elution with ethyl acetate (75 m*l*×3) gave 679 mg of a sticky material which gave 40 mg of an inorganic perchlorate salt by the addition of 30 m*l* of ethyl acetate to the residue. The solid was filtered off and after the solvent was removed under vacuo, the residue was dissolved in small amount of methylene chloride. By the addition of ether and ethanol to the methylene chloride solution, was obtained 148 mg of solid which was recrystallized from the mixture of acetonitrile and ether to give 78 mg (0.20 mmol) of 5: mp (dec) 180-181°C. Finally elution with acetone gave 1.372 g of sticky material which was treated with water to give 1.074 g (2.63 mmol) of white solids, identified as 10.

Reaction of 1 *with* 6 *in the argon atmosphere.* This reaction was run in the same scale as in the reaction in the air. In this case, 12 was not detected even on thin layer chromatogram. Instead, 20 mg (0.086 mmol) of 3 was obtained. *cis*-Thianthrene-5,10-dioxide (34 mg, 0.14 mmol) was obtained along with other compounds as in the reaction in the air.

Reaction of 1 *with* 9 *in the argon atmosphere.* To a solution of 1.104 g (3.49 mmol) of 1 in 25 ml of acetonitrile was added 1.235 g (3.49 mmol) of the azo compound (9). After the mixture was stirred for 3 hours, the solvent was removed under vacuo and the residue was chromatographed on a silica gel column (12×2cm). Elution with hexane (600 m*l*) gave 516 mg (2.39 mmol) of 2. Elution with benzene (75 m*l*×2) gave 180 mg (0.46 mmol) of the unreacted azo compound (9). Next benzene fractions (75 m*l*×5) afforded 626 mg (4.50 mmol) of p-nitrophenol and 9 mg of 3. Other benzene fractions (75 m*l*×2) yielded 22 mg (0.089 mmol) of 4. Elution of ethyl acetate (75 m*l*×3) gave 498 mg of dark brown solid which was recrystallized from the mixture of acetonitrile and ether to give mp (dec) 202-204°C. However, the structure of the compound

TABLE 1: Summary of the Reactions of 1 with the Azo Compounds 6 and 9

Reactants (mmol)			Atm	Products (mmol)								
1	6	9		2	3	4	12	10	11	5	[c]	[d]
5.98	5.98		Air	4.09		0.22		1.21	0.31	0.12	8.65	
6.85	1.28		Air	3.39		0.16	0.048	2.63		0.20		
6.85	1.28		Ar		0.086	0.14				[a]		
3.49		3.49[b]	Ar	2.39	0.04	0.089			0.42	[a]		4.50

[a] Trapping experiments of acetone were not carried out. [b] Recovered *9* was 0.46 mmol (13%). [c] Phenol. [d] p-nitrophenol.

has not been determined. Acetone fraction (70 ml) gave 260 mg of sticky brown material, which was decolorized, followed by recrystallization from acetonitrile-ether, yielding 151 mg (0.42 mmol) of **11**.

Results

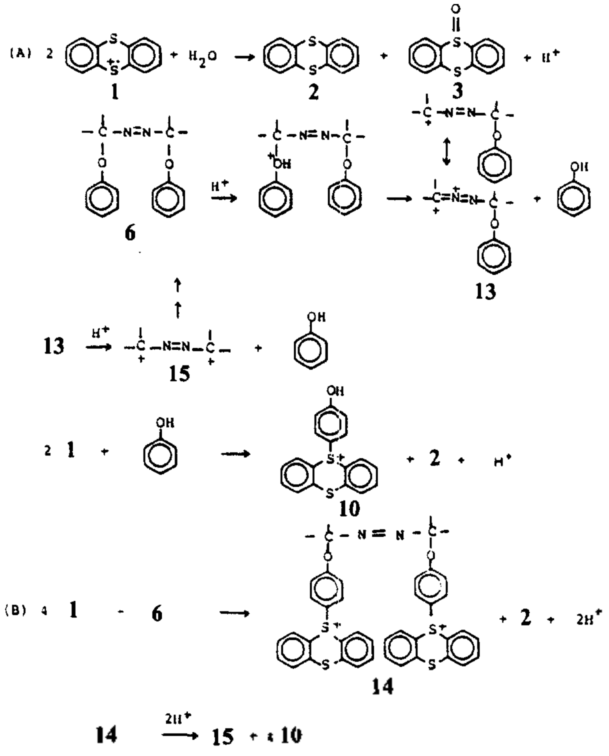
Thianthrene cation radical perchlorate (**1**) reacts rapidly with azo-bis-2-phenoxy-2-propane (**6**) and azo-bis-2-(p-nitrophenoxy)-2-propane (**9**) at room temperature. When the mole ratio of two starting materials is 1:1, common products in both reactions are thianthrene (**2**), *cis*-thianthrene-5,10-dioxide (**4**), 5-acetonylthianthrenium perchlorate (**5**), and 5-(2-propenyl) thianthrenium perchlorate (**11**) which has never been reported. Table 1 shows the results.

This reaction was dependent on the concentration of the azo compound. The alkenesulfonium salt (**11**) was not formed when the azo compound was added until the color of the cation radical (**1**) had disappeared, which appeared when the mole ratio of **1** to the azo compound was about 5:1.

The formations of **4** and **12** suggest that a peroxy radical was involved during the reaction (vide infra). Therefore, the reaction was carried out in argon atmosphere. Only difference between in the argon atmosphere and in the air was isolation of small amount of **3** instead of **12**.

Discussion

Unexpectedly, **1** reacted rapidly with **6** at room temperature. No azo compound with thianthrene moiety was found. The isolation of **10** and large amounts of phenol suggested two plausible pathways for the decomposition of the azo compound (**6**), which were summarized in Scheme 1.



Scheme 1.

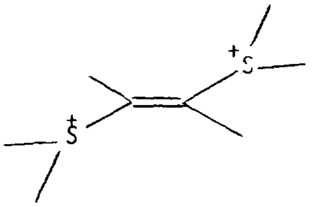
Path (A) shows protonation on oxygen of a phenoxy group, followed by dissociation to form azo cation (**13**) and phenol which then reacts with **1** to form **10**. It is reasonable to assume that protons are generated in the reaction of **1** with water which still remains in dried acetonitrile according to the known stoichiometry.[8] The fact that about 10 mg of **3** is almost always formed in about 30 ml of dried acetonitrile supports the above statement.

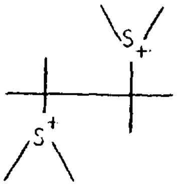
In order to see if **6** decomposes to generate phenol by the acid, 10 μl of 70% $HClO_4$, which was the calculated amount of perchloric acid to be generated in imperfect dried acetonitrile was added to a 10^{-4}M of **6** in acetonitrile at −15°C and ultraviolet spectrum was recorded in every two minutes. The peaks at 263 and 279 nm due to the absorption by phenol showed continually increased intensities in place of those at 260 and 265 nm of **6**. Therefore, the spectral change supports the dissociation of phenol by perchloric acid.

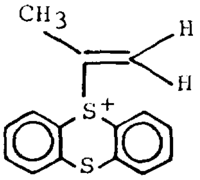
The azo cation (**13**) formed concomitantly with phenol was originally proposed by Benzig in the solvolysis of azo-bis-2-chloro-2-propane (**8**) in aq. acetone[9] and in chlorination of acetone ketazine by McBride and co-worker.[10] Since **6** is synthesized by the displacement of chlorine of **8** with phenoxide, the formation of **13** is a retroreaction to the synthesis of **6**.

In the case of path (B), it was assumed that **1** reacted with phenoxy groups of **6** in the first step. This was based on the facts that **1** reacted smoothly with aromatics with electron-donating groups such as phenol,[6] anisole,[6] and dibenzo-18-crown-6.[11] We do not have any direct evidence for the formation of disulfonium salt (**14**) from **6**. If **1** reacted first with phenoxy groups prior to the formation of phenol, it would be expected that azo-bis-2-(p-nitrophenoxy)-2-propane (**9**) could not react with **1**. However, the reverse was the case. Table 1 showed similar results to those obtained without having nitro group except for the formation of p-nitrophenol, which did not react with **1** since nitro group deactivated the ring. Therefore, path (A) is more favorable to path (B). In the meantime, Benzig[2] described the conversion of **6** to acetone in the presence of water, which, in our cases, was confirmed by the isolation of 5-acetonylthianthrenium perchlorate (**5**).[7] When the mole ratio of **1** to **6** was 1:1, **5** was isolated by the addition of **1** to the solvent trapped at −78°C. On the other hand, when the corresponding ratio was about 5:1, the same compound was isolated by the column chromatography of the reaction mixture. In other word, acetone was formed in both cases. It existed in the solvent without forming **5** for the former but for the latter it transformed to **5**. This difference is simply due to the fact that the reaction with phenol is much faster than that with acetone.[12] Since 2 moles of phenol is formed from 1 mole of **6**, only **10** is expected from the reaction with 1 mole of **1**. Therefore, excess phenol and acetone formed exist in the solvent. On the contrary, when 5 moles of **1** are used 4 moles of **1** reacts with 2 moles of phenol and the rest of **1** can participate in the reaction with acetone to lead **5**.

Recently Shine and co-workers reported the reaction of **1** with several alkynes and olefins.[13] From the reactions with alkynes and olefins were obtained vinylidendisulfonium salts and alkanedisulfonium salts, respectively.







11

We have isolated a vinylidenemonosulfonium salt, *i.e.*, 5-(2-propenyl)thianthrenium perchlorate (11) when the mole ratio of **1** to the azo compounds, **6** and **9**, was 1:1. There have been many reports about alkenemonosulfonium salts.[14] However, to our knowledge, this is the first example for the formation of alkenemonosulfonium salt from the reaction with cation radical. The formation mechanism of this compound may be quite different from that of the disulfonium salt.[13] Apparently **11** cannot be formed from the reaction with either propyne[13] or propene. Furthermore, it was not formed from the coupling reaction between 2-propenyl radical and **1**.[15] Preliminary investigation revealed that the yield of **11** was somewhat increased in the light of **5** when this reaction was run in the vacuum line. This resut indicates that the azo cation (13) acts as an intermediate leading to both compounds, *i.e.*, **5** and **11**. At this moment, we do not know the fate of **13**. The azo cation (13) might undergo further reaction to give phenol and **15** which lost protons to form azo-bis-2-propene. This possibility are currently under investigation.

The formation of **3** was often observed in the reaction with **1** as mentioned before but those of **4** and **12** appeared only in a few cases.[1,12,16] The significance of these compounds on the reaction mechanism was previously proposed.[17] We believe that a radical is somehow involved in these reactions. Thianthrene persulfoxide, which is believed to be formed from the reaction of **1** with a peroxy radical transforms to **3**, **4**, and **12**. According to Ohno and co-worker's result on homolysis of **6** in diphenyl ether at 160°C,[18] the major compound was acetophenone, which was resulted from the rearrangement, followed by bond scission of 2-phenoxy-2-propyl radical. Their reaction condition was very much different from that of ours and no acetophenone or acetophenone derived sulfonium salt was obtained. Therefore, it is unlikely that 2-phenoxy-2-propyl radical is a precursor of peroxy radical. Research to solve this mechanistic problem is in progress.

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