Cation Radicals with 2-Pyridylhydrazones in Nitrile Solvents *s*-Triazolo[4,3-*a*]pyridines by Thianthrene Cation Radical Perchlorate and 1-(2-Pyridyl)-1,2,4-Triazoles by Tris(2,4-Dibromophenyl)-aminium Hexachloroantimonate

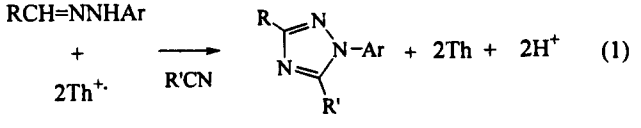
Koon Ha Park[†*], Kun Jun[††], Seung Rim Shin[‡], and Sea Wha Oh[‡]

[†]*Department of Chemistry, Chungnam National University, Taejon 305-764, Korea*
[‡]*Korea Research Institute of Chemical Technology, P.O. Box 107, Taejon 305-606, Korea*
Received February 13, 1997

Reactions of arenealdehyde 2-pyridylhydrazones (**1**) with thianthrene cation radical ($Th^{+\cdot}$) and tris(2,4-dibromophenyl)aminium hexachloroantimonate ($Ar_3N^{+\cdot}$ $SbCl_6^-$) were investigated. The major product was switched depending on the cation radical being used. That is, *s*-triazolo[4,3-*a*]pyridines (**2**), an intramolecular cyclization product, and 1-(2-pyridyl)-1,2,4-triazoles (**3**), an intermolecular cycloaddition product, were obtained as a major product when reacted with $Th^{+\cdot}$ and $Ar_3N^{+\cdot}$, respectively in nitrile solvents. The plausible mechanisms are proposed based on both the reduction potentials of $Th^{+\cdot}$ and $Ar_3N^{+\cdot}$ and control experiments.

Introduction

The chemistry of thianthrene cation radical ($Th^{+\cdot}$) has been investigated with a variety of substrates and it has been well documented that the reactions of $Th^{+\cdot}$ with nucleophiles take place usually at the sulfur atom and sometimes at a ring carbon.[1] Reactions of $Th^{+\cdot}$ with arylhydrazones of benzaldehyde,[2] chalcone and benzalacetone[3] have been reported to give oxidative cycloaddition products to nitrile solvents to form 1,2,4-triazoles (Eq. 1) and oxidative intramolecular cyclization to pyrazoles (Eq. 2), respectively.



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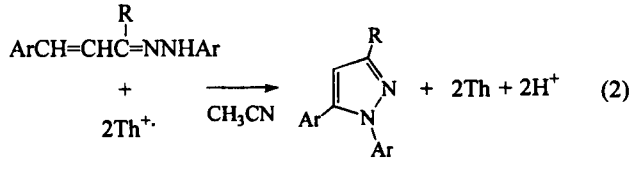

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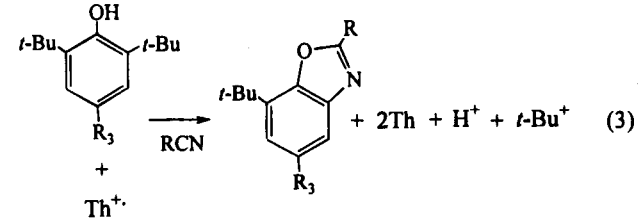

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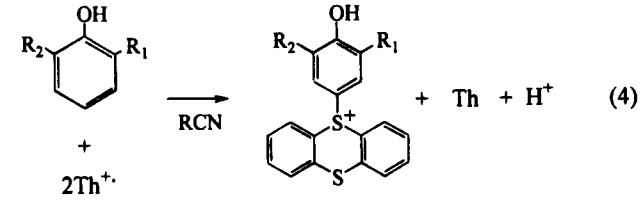


(4)

On the other hand, reactions of $Th^{+\cdot}$ with phenol derivatives showed complicated reaction pathways depending on substituents in the aromatic ring (Eq. 3 and 4).[4]

In this regards, recent report of phenolic Schiff's bases with $Th^{+\cdot}$ has shown the formation of 2-arylbenzoxazoles by an intramolecular participation of the phenolic OH in the cyclization, instead of the expected intermolecular cyclization and nucleophilic substitution.[5] Herein, the reactions of arenealdehyde 2-pyridylhydrazones (**1**) with $Th^{+\cdot}$ and $Ar_3N^{+\cdot}$ in nitrile solvents are reported. The purpose of the present studies is to see how the pyridyl nitrogen might participate in the reaction, if it shows any reactivity.

Experimental

General

Nitrile solvents such as acetonitrile, acrylonitrile, and propionitrile (Aldrich HPLC grade) were dried by distillation over phosphorus pentoxide under argon prior to use. Thianthrene (Aldrich) was recrystallized twice from acetone. All aldehydes, hydrazines, and acid chlorides were used without further purification.

2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) (Aldrich) was purified by sublimation. All inorganic chemicals were used without further purification.

Chromatographic Techniques

Merck silica gel sheet (silica gel 60 F_{254}) was used for diagnostic thin layer chromatography, preparative thin layer chromatography was carried out with Merck 2 mm silica gel plates (silica gel 60 F_{254}). Column chromatography was performed on Merck silica gel (Grade 60, 230-400 mesh, 60A). Gas chromatography (GC) was carried out on a Hewlett Packard 5890 series. The following columns were used: A; DB-1 capillary column (30 m × 0.25 mm). B; DB-5 capillary column (30 m × 0.25 mm). C; DB-1 capillary column (30 m × 0.53 mm).

Quantitative analysis of products by GC was done with the use of authentic compounds and biphenyl as an internal standard. Calculations were made as follows;

Concentration factor (C_F) of a compound
$$= \frac{\text{Peak area (from GC integration) of the compound}}{\text{Amount of the compound (in mmol)}}$$

Response factor (R_F) of a compound
$$= \frac{C_F \text{ of the compound}}{C_F \text{ of the internal standard}}$$

Amount of a compound (in mmol)
$$= \frac{\text{Peak area of the compound}}{(R_F \text{ of the compound}) \times (C_F \text{ of the internal standard})}$$

Spectroscopic Techniques

^{1}H NMR spectra were recorded with 300 MHz IBM-Bruker spectrometer. ^{1}H NMR chemical shifts were measured in ppm relative to tetramethylsilane. The coupling constants (J) were measured in Hz. High resolution mass spectra (HRMS) were determined with JEOL JMS-DX 303. Mass spectra (GC-MS) were obtained either on a Varian Saturm II GC-Mass spectrometer or on a Shimadzu QP 1000 Mass spectrometer. Infrared (IR) spectra were recorded on a Analet FX 60 FT-IR spectrometer. All elemental analyses were performed by FISONS EA1108.

Thianthrene Cation Radical Perchlorate

By following the known procedure,[6] thianthrene cation radical perchlorate was prepared.

Thianthrene 5-Oxide (ThO)

By following the known procedure,[7] thianthrene 5-oxide was prepared. mp 140-141 °C (lit.[7] mp 143.0-143.5 °C).

Tris(2,4-dibromophenyl)aminium Hexachloroantimonate

By following the known procedure,[8] tris(2,4-dibromophenyl)aminium hexachloroantimonate was prepared.

Preparation of Hydrazones (1a-d)

All the hydrazones are known compounds except **1d** and were prepared according to the known procedure.[9]

Benzaldehyde 2-Pyridylhydrazone (1a). A solution of benzaldehyde (3.20 g, 30 mmol) and 2-hydrazinopyridine (5.01 g, 46 mmol) in ethanol (20 mL) containing glacial acetic acid (5% by wt. to the amount of the aldehyde) was boiled under reflux for 3 h. Upon cooling, the hydrazone precipitated as a pale yellow solid. Recrystallization from ethanol gave pale yellow crystals (4.50 g, 22.8 mmol, 76%). mp 149-150 °C (lit.[9] 148 °C).

4-Methylbenzaldehyde 2-Pyridylhydrazone (1b). By following the similar procedure as was described for **1a**, pale yellow crystals (5.0 g, 23.7 mmol, 79%) were obtained from 4-methylbenzaldehyde (3.60 g, 30 mmol) and 2-hydrazinopyridine (4.20 g, 37.5 mmol). mp 162-163 °C (lit.[10] 153 °C).

4-Nitrobenzaldehyde 2-Pyridylhydrazone (1c). By following the similar procedure as was described for **1a**, bright yellow crystals (4.80 g, 19.8 mmol, 66%) were obtained from 4-nitrobenzaldehyde (4.53 g, 30 mmol) and 2-hydrazinopyridine (5.00 g, 46 mmol). mp 225-227 °C (lit.[10] 220 °C).

4-Bromobenzaldehyde 2-Pyridylhydrazone (1d). By following the similar procedure as was described for **1a**, pale yellow crystals (6.40 g, 23.2 mmol, 77%) were obtained from 4-bromobenzaldehyde (5.50 g, 30 mmol) and 2-hydrazinopyridine (5.00 g, 46 mmol).

mp 194-195 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.96 (s, 1H), 8.11-8.09 (m, 1H), 7.96 (s, 1H), 7.65-7.55 (m, 5H), 7.23 (d, 1H, J=8.4), 6.78-6.74 (m, 1H). GC/MS: m/e (relative intensity): 277 (M+2, 57.6), 275 (M^+, 59.3), 120 (40.8), 94 (100), 67 (38.3). HRMS: Calcd. for $C_{12}H_{10}N_3Br$, 275.0058; found, 275.0058.

General Reactions of Thianthrene Cation Radical ($Th^{+\cdot}$) with Heterocyclic Hydrazones in Nitrile Solvents

Hydrazone (0.5 mmol) and $Th^{+\cdot}$ (1.0 mmol) were placed in a septum-capped flask, evacuated, filled with argon, and nitrile solvent (20 mL) was added to the flask with a syringe. The mixture was stirred for 24 h at room temperature and water (10 mL) was added, followed by neutralization with dilute sodium bicarbonate solution. The organic product mixture was extracted with methylene chloride (5×30 mL) and the solvent was dried over anhydrous sodium sulfate. After filtration, the combined organic layer was concentrated using a rotary evaporator. The solid residue was dissolved in methylene chloride (50 mL) and was used for identification of products by GC and GC/MS, and for quantitative analysis by GC. Authentic samples were used as controls. The products were separated by preparative TLC using methylene chloride/methanol (15 : 2, v/v) as the developing solvent, removed from the plate and extracted with methylene chloride. The separated products were identified by GC/MS, ^{1}H NMR, melting point, elemental analysis, HRMS and comparison with authentic samples. Each reaction was carried out twice. A summary of products and yields are listed in Table 1.

General Reactions of Tris(2,4-dibromophenyl)aminium Hexachloroantimonate with Heterocyclic Hydrazones in Nitrile Solvents

Similar procedure as described in the general reactions of thianthrene cation radical was followed, except the use of tris(2,4-dibromophenyl)aminium hexachloroantimonate instead of thianthrene cation radical.

Preparation of Authentic Compounds

The known triazolopyridines **2a-c** and triazole **3a** were prepared according to the previous procedure.[10b] The new **2d** and **3b-g** were obtained from the corresponding reactions of **1** and cation radicals and were used as authentic compounds after purification. Physical properties of the new compounds, **2d** and **3b-g**, are as follows.

3-(4-Bromophenyl)-*s*-triazolo[4,3-a]pyridine (2d). Similar procedure as reported previously was followed.[10b] From 0.50 g (1.81 mmol) of **1d** and 0.85 g (1.83 mmol) of lead tetraacetate, 0.21 g (0.77 mmol, 42%) of colorless crystals was obtained after recrystallization from ethanol/acetone (1 : 1, v/v).

mp 195-196.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (d, 1H, J=9.3), 7.76 (d, 1H, J=7.0), 7.73 (s, 4H), 7.34-7.27 (m, 1H), 6.93-6.89 (m, 1H). GC/MS: m/e (relative intensity); 275 (M+2, 91.5), 274 (M+1, 100), 273 (M^+, 70.3), 102

(7.3), 65 (8.2). HRMS. Calcd. for $C_{12}H_8N_3Br$, 272.9906; Found, 272.9907.

1-(2-Pyridyl)-3-(4-methylphenyl)-5-methyl-1,2,4-triazole (3b). mp 97.5-98 °C (ethanol/acetone). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.49 (d, 1H, *J*=4.8), 8.07 (d, 2H, *J*=8.2), 7.99 (d, 1H, *J*=8.2), 7.89 (td, 1H, *J*=7.8, 1.9), 7.29-7.25 (m, 3H), 2.93 (s, 3H), 2.40 (s, 3H). GC/MS: m/e (relative intensity); 250 (M^+, 100), 208 (34.6), 133 (22.9). Elemental analysis: Found; C (72.33), H (5.59), N (22.51). Anal. Calcd. for $C_{15}H_{14}N_4$; C (72.00), H (5.60), N (22.40).

1-(2-Pyridyl)-3-(4-bromophenyl)-5-methyl-1,2,4-triazole (3d). mp 139-140 °C (ethanol/acetone). ^1H NMR (300 MHz, $CDCl_3$): 8.50 (ddd, 1H, *J*=4.9, 1.8, 0.8), 8.04 (d, 2H, *J*=8.7), 7.97 (d, 1H, *J*=8.2), 7.88 (td, 1H, *J*=7.7, 1.9), 7.58 (d, 2H, *J*=8.7), 7.29 (ddd, 1H, *J*=7.3, 4.8, 1.1), 2.93 (s, 3H). GC/MS: m/e (relative intensity); 316 (M+2, 98.0), 314 (M^+, 100), 274 (49.5), 133 (75.4), 102 (18.4), 78 (26.1), 65 (36.2), 51 (50.2). HRMS. Calcd. for $C_{14}H_{11}N_4Br$, 314.0180; Found, 314.0181.

1-(2-Pyridyl)-3-(4-bromophenyl)-5-ethyl-1,2,4-triazole (3e). mp 100.5-101.5 °C (ethanol/acetone). ^1H NMR (300 MHz, $CDCl_3$): 8.50 (d, 1H, *J*=4.9), 8.06 (d, 2H, *J*=8.8), 7.97-7.85 (m, 2H), 7.58 (d, 1H, *J*=8.6), 7.31-7.27 (m, 1H), 3.56 (q, 2H, *J*=7.5), 1.42 (t, 3H, *J*=7.5). GC/MS: m/e (relative intensity); 331 (M+3, 98.8), 329 (M+1, 100), 328 (M^+, 15.5), 146 (11.4). HRMS. Calcd. for $C_{15}H_{13}N_4Br$, 328.0325; Found, 328.0325.

1-(2-Pyridyl)-3-phenyl-5-vinyl-1,2,4-triazole (3f). mp 45-47 °C (benzene/cyclohexane). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.53 (ddd, 1H, *J*=4.9, 1.8, 0.8), 8.23 (dd, 2H, *J*=8.0, 1.7), 7.98 (d, 1H, *J*=8.2), 7.89 (td, 1H, *J*=7.7, 1.9), 7.67 (dd, 1H, *J*=17.4, 11.1), 7.49-7.43 (m, 3H), 7.34 (ddd, 1H, *J*=7.3, 4.9, 1.2), 6.62 (dd, 1H, *J*=17.4, 1.7), 5.75 (dd, 1H, *J*=11.0, 1.7). GC/MS: m/e (relative intensity); 248 (M^+, 66.4), 247 (M-1, 100), 207 (11.1), 194 (33.7), 144 (11.9), 78 (15.5), 65 (23.0), 49 (46.8). Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.58; H, 4.84; N, 22.58. Found: C, 72.26; H, 5.10; N, 22.06.

1-(2-Pyridyl)-3-(4-bromophenyl)-5-vinyl-1,2,4-triazole (3g). mp 104-107 °C (ethanol/acetone). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.55 (d, 1H, *J*=4.6), 8.11 (d, 2H, *J*=8.4), 7.98-7.89 (m, 2H), 7.67 (dd, 1H, *J*=17.4, 10.9), 7.60 (d, 2H, *J*=8.4), 7.36-7.32 (m, 1H), 6.61 (dd, 1H, *J*=17.4, 1.7), 5.76 (dd, 1H, *J*=11.0, 1.7). GC/MS: m/e (relative intensity); 328 (M+2, 35.4), 327 (M+1, 100), 326 (M^+, 32.8). HRMS. Calcd. for $C_{15}H_{11}N_4Br$, 326.0172; Found, 326.0173.

Results and Discussions

Reactions of 2-pyridylhydrazones (**1a-d**) with cation radicals such as $Th^{+\cdot}$ and $Ar_3N^{+\cdot}$ were carried out in nitrile solvents and the results are listed in Table 1.

The results in Table 1 clearly show that the major product was switched depending on the cation radicals being used. That is, reactions of **1a-d** with $Th^{+\cdot}$ proceeded mainly by oxidative intramolecular cyclization to give *s*-triazolo[4,3-*a*]pyridines (**2a-d**), while with $Ar_3N^{+\cdot}$, 1,2,4-triazoles (**3a-g**) were obtained by cycloaddition to nitrile solvents (Scheme 1).

In these reactions none of the nucleophilic substitution products such as thianthreniumyl perchlorates was obtained, contrary to the previous reports that pyridine as a nucleophile had attacked $Th^{+\cdot}$ to make *N*-(2-thianthrenyl)pyridine perchlorate.[1b]

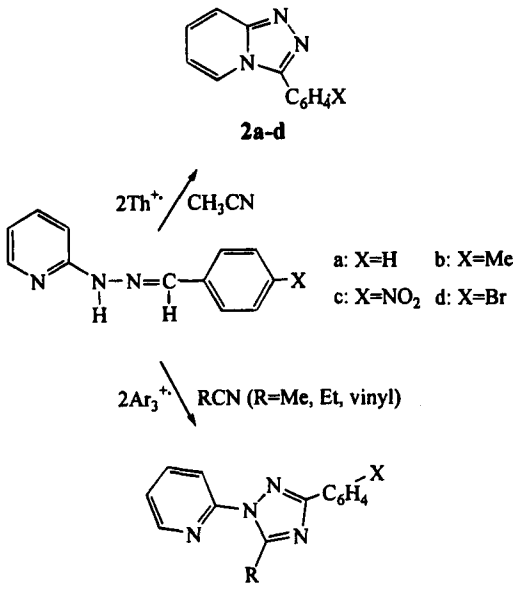
The intramolecular cyclization of **1** to **2** had been performed with a variety of oxidizing agents[10a] and anodic oxidation.[11] However, the formation of **3** has been known only by anodic oxidation, in which **3** (10%) was obtained as a minor product along with **2** (62%).[11b]

In the reactions of **1** with $Th^{+\cdot}$ in acetonitrile, excellent yields of **2** with small amounts of **3** were obtained (Table 1). The other products observed in our reactions were Th as a redox partner product and ThO. Formation of ThO is not related to the main reaction but stems from the hydrolysis of $Th^{+\cdot}$ due to either adventitious water or water added in the work-up procedure.

Table 1. Quantitative Analysis of Products in the Reactions of Pyridylhydrazones **1** with Cation Radicals in Nitrile Solvents

Run	X	Solvent	Cation Radical[a]	Products, Yield %					
				Th[b]	ThO[b]	Ar_3N	**2**[c]	**3**[d]	**1**
1	H	CH_3CN	A	88.5	5.3		92	5.8	
2[e]	H	CH_3CN	A	90.0	4.9		81.2		6.9
3	Me	CH_3CN	A	97.4			73.0	27.8	
4[e]	Me	CH_3CN	A	87.0	12.7		72.4	trace	26.8
5	NO_2	CH_3CN	A	88.1	9.4		82.0		12.8
6[e]	NO_2	CH_3CN	A	98.1	1.0		94.4		2.8
7	Br	CH_3CN	A	88.4	8.5		93.4	2.2	1.3
8[e]	Br	CH_3CN	A	96.5	3.4		89.9		6.4
9	H	CH_3CN	B			89.4	16.8	73.9	0.2
10	H	CH_2=CHCN	B			86.1	16.7	41.7	0.4
11	H	C_2H_5CN	B			85.7	17.4	62.6	7.0
12	Me	CH_3CN	B			84.7	20.6	66.6	3.4
13	Br	CH_3CN	B			96.6	12.7	82.9	2.0
14	Br	C_2H_5CN	B			92.9	8.0	78.0	7.6
15	Br	CH_2=CHCN	B			81.0	14.8	58.6	

[a] A=$Th^{+\cdot}$ ClO_4^-; B=$(2,4\text{-}Br_2C_6H_3)_3N^{+\cdot}$ $SbCl_6^-$. [b] Based on the amount of $Th^{+\cdot}$. [c] Characterized by ^1H NMR, GC/MS, and mp, and by comparing those of authentic samples. [d] Characterized by ^1H NMR, GC/MS, and elemental analyses. [e] In the presence of 1.5 eq of DTBMP.



Scheme 1.

As a control experiment, **1a** was treated with aqueous perchloric acid (*ca.* 70%) in acetonitrile, but any cyclized product was not observed. This observation indicates that the products obtained in our reactions are not derived from the acid liberated during the reaction.

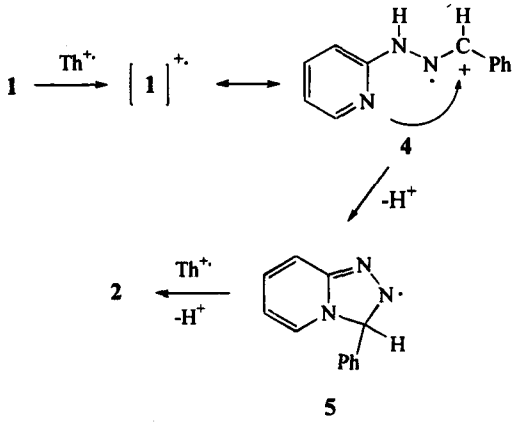
Reactions of **1** with $Ar_3N^{+\cdot}$ proceeded rapidly and gave unexpectedly the intermolecular cycloaddition product **3** as a major product together with **2**. Oxidation with $Ar_3N^{+\cdot}$ led to the formation of Ar_3N as a redox partner product.

The results in Table 1 can be understood in the light of intrinsic differences in chemical behaviors of the two cation radicals. One of the criteria is the reduction potential of $Ar_3N^{+\cdot}$ (1.5 V *vs* SCE),[12a] $Th^{+\cdot}$ (1.3 V *vs* SCE),[10b] and oxidation potential of **1a** (1.2 V *vs* SCE).[11b] As far as the reduction potentials are concerned, $Ar_3N^{+\cdot}$ would be stronger oxidant than $Th^{+\cdot}$. These different oxidizing capabilities of the cation radicals are manifested in the formation of **2** and **3**.

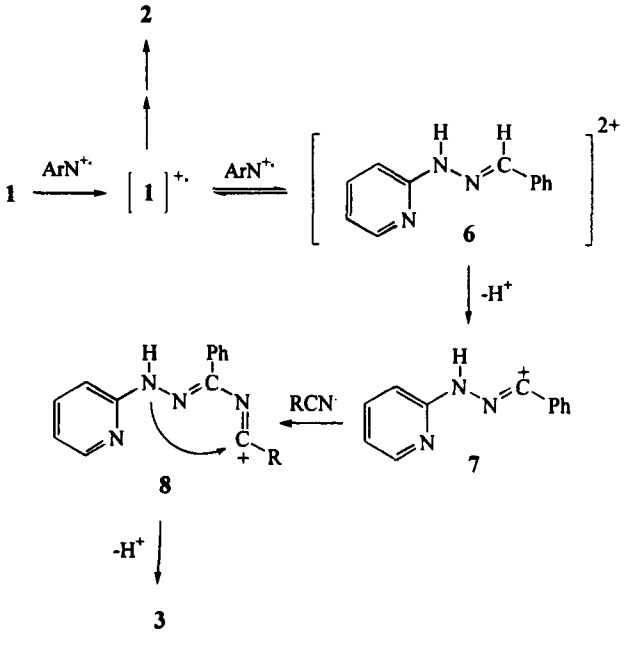
In the reaction of **1** with $Th^{+\cdot}$, the formation of major product **2** is suggested in Scheme 2. Herein the intermediate **4** which was formed by one electron oxidation of **1** gave mainly **5** by an intramolecular cyclization and the successive deprotonation. Intramolecular 1,5-cyclization would be much faster than intermolecular cycloaddition with acetonitrile. A second oxidation and deprotonation would convert **5** to **2**.

In the reaction of **1** with $Ar_3N^{+\cdot}$, **3** was obtained as a major product along with **2** as a minor one (Scheme 3).

A plausible pathway for this transformation is as follows. That is, a dication **6** which was formed by stronger oxidant $Ar_3N^{+\cdot}$ would generate a nitriliminium ion **7**. The reaction of nitrile solvent and the nitriliminium ion **7** (Ritter reaction) would yield the intermediate **8** which can be converted to product **3**.



Scheme 2.



Scheme 3.

The presence of a nitriliminium ion **7** was evidenced from the reaction of **1a** with $Ar_3N^{+\cdot}$ in acrylonitrile (run 10 in Table 1). As reported previously, pericyclic cycloadditions of nitrilimine to acrylonitrile is known to occur at vinyl rather than at the nitrile group.[14] Accordingly, the formation of 5-vinyl-1,2,4-triazole in our reaction provided a supporting evidence that the reaction of **1** with $Ar_3N^{+\cdot}$ goes through a stepwise pathway rather than a pericyclic cycloaddition route. In addition, the mechanisms in Scheme 2 and 3 are based on control experiments. One was the reaction of **1a** with $SbCl_5$ in acetonirile to get some amounts of **2** and other unidentified products free from **3**. The other was the use of tris(4-bromophenyl)aminium hexachloroantimonate (1.05 V *vs* SCE),[13] which has lower reduction potential than that of $Th^{+\cdot}$. Compound **2** was obtained as a major product but **3** was not detected. The two results were in favor of the proposed mechanisms shown in Scheme 2 and 3.

Usually 1,2,4-triazoles have been prepared by 1,3-dipolar cycloaddition of nitrilimines and nitriliminium ions, which are generated from hydrazinoyl chloride[14] by the action of

triethylamine or aluminum chloride.[15] Compared with the known procedures, the present method of using cation radicals is simpler and more efficient.

Acknowledgments. Financial support from the Organic Chemistry Research Center sponsored by Korea Science & Engineering Foundation (1996) and the Ministry of Education through the Basic Science Research Institute Program (BSRI-96-3433) is gratefully acknowledged.

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Preparation and Photoluminescence Properties of the $ZnGa_2O_4$:Mn Phosphor by Polymerized Complex Precursor

Du-Hwan Jo, Ha-Kyun Jung, Sang-Il Seok, and Do-Soon Park*

Korea Research Institute of Chemical Technology, Taejon 305-600, Korea
Received February 19, 1997

The preparation and photoluminescence properties of $ZnGa_2O_4$:Mn phosphor are presented. Under 254 nm excitation $Zn_{1-x}Mn_xGa_2O_4$ exhibits the green emission band at 506 nm wavelength and maximum intensity where x=0.005. The manganese activated $ZnGa_2O_4$ phosphor prepared by the polymerized complex method shows a remarkable increase in the emission intensity and is smaller particle size than that prepared by conventional method. Also, electron paramagnetic resonance study on $ZnGa_2O_4$:Mn powders indicates that the increase in emission intensity after firing treatment in mild hydrogen reducing atmosphere is due to the conversion of the higher valent manganese to Mn^{2+}.

Introduction

In the past few years special attention has been paid to $ZnGa_2O_4$ based phosphors due to their potential applications as luminescent materials in flat panel displays (FPDs), electroluminescent (EL) devices and AC plasma (ACP) panels.[1] A current research interest in the area of luminescence and display technologies is the development of both novel and improved phosphor synthesis techniques. High resolution, short decay time, high brightness, and high efficiency are the major requirements of phosphors used in flat panel display devices such as field emission displays (FEDs).[2]

The $ZnGa_2O_4$ phosphor has been studied for its good luminescent charateristics at low voltage. The $ZnGa_2O_4$ is a compound oxide of ZnO and Ga_2O_3 as the spinel structure, and optical band gap is about 4.4 eV. Also, the results of high temperature operating lifetime test have been proven to show the excellent stability of this phosphor. In addition,