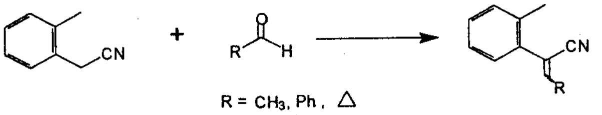
Benicewieg, B. C. *Synthesis* **1994**, 675.
15. The following transformation was successfully acheived by untilizing KF-alumina in our laboratory.



16. All compounds were isolated and fully characterized by spectroscopic methods. For example: Compound **10** ^1H NMR (200 MHz, $CDCl_3$) δ 5.20 (t, 1H, J=6.9), 5.10 (m, 1H), 3.07 (d, 2H, J=6.9), 2.08 (m, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H) Compound **13** ^1H NMR (200 MHz, $CDCl_3$) δ 6.11 (s, 1H), 6.09 (s, 1H), 5.10 (t, 1H), 5.34 (m, 1H, J=8.8), 3.38 (ddd, 1H, J=8.8, 7.6, 7.4), 2.91 (ABq, 1H, J=7.4, 7.2), 2.73 (ABq, 1H, J=7.6, 7.2), 2.26 (s, 3H), 2.04 (m, 4H), 1.66 (s, 3H), 1.66 (s, 3H), 1.58 (s, 3H).

Oxidation of Aromatic Ketone Hydrazones by Thianthrene Cation Radical

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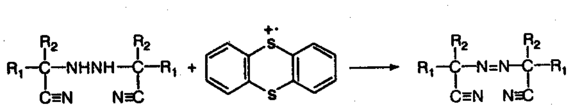
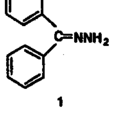
Recently we have reported the efficient, cation radical-induced, oxidation of hydrazonitriles to the corresponding azo compounds (eq 1).[1] But an unstable azoalkane, 3,6-dicyano-3,6-dimethyl-1,2-diazacyclohexene, decomposed to give the cleavage product, methacrylonitrile and the coupled product, trans-1,2-dicyano-1,2-dimethylcyclobutane with nitrogen evolution. With the view of increasing the scope of this cation radical-induced oxidation, we successfully investigated the transformation of aromatic ketone hydrazones into diazo compounds.

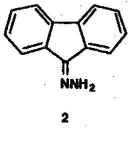


(1)

We now report a new oxidation of four unsubstituted aromatic ketone hydrazones induced by thianthreniumyl perchlorate ($Th^{+}\cdot ClO_4^-$): bezophenone hydrazone **1**, 9-fluorenone hydrazone **2**, benzil monohydrazone **3**, and benzil dihydrazone **4**.



1



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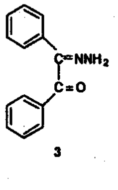

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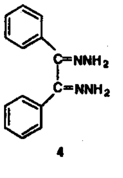


4

Table 1. Oxidation of Ketone Hydrazones to Diazo Compounds by Thianthrene Cation Radical[a]

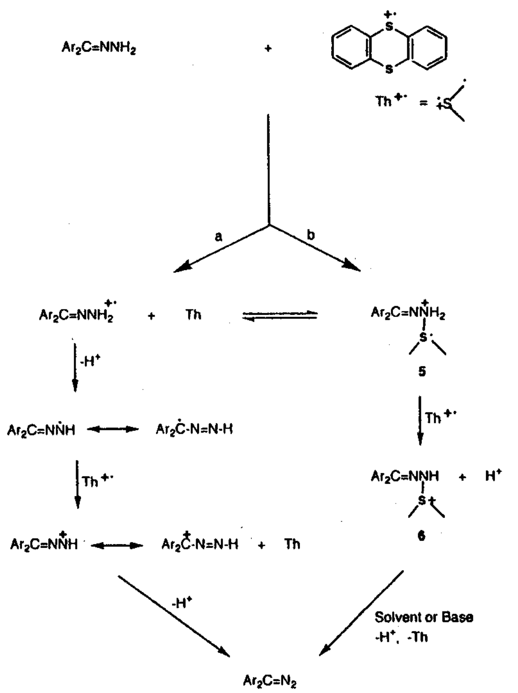
Run	Ketone hydrazone[b]	Yields (%)[b] 7	8	9	12	Th	ThO
1	**1**	94				90	2
2	**2**		75			80	4
3	**3**			80		83	2
4[c]	**4**				74	86	7

[a] Oxidation was carried out by general procedure. Solid $Th^{+}\cdot ClO_4^-$ and ketone hydrazone in the mole ratio 2 : 1 were placed under argon in a septum-capped flask into which 20 mL of acetonitrile was injected by syringe. The dark purple color of $Th^{+}\cdot$ disappeared with time, but the solution was stirred overnight. Water (5 mL) was then added, the solution was neutralized with $NaHCO_3$ and extracted repeatedly with CH_2Cl_2 (4×20 mL) and the dried CH_2Cl_2 solution was evaporated. The residue thus obtained was taken up in a standard volume of CH_2Cl_2, and the solution was analyzed. [b] Each reaction was run twice, and the averaged yiels of products are given. Products were identified and quantified by GC, using the method of "standard addition" of authentic samples,[19] and by ^1H NMR and GC/MS. GC analysis employed a 2 m×1/8 in. 10% OV-101/Chrom W packed column programmed from 50 to 250° at 10 deg/min. The ketone hydrazones and the four products were prepared by standard procedures as referenced and had satisfactory GC/MS, NMR, and other data. [c] The mole ratio of cation radical to **4** was 4 : 1.

The oxidation of ketone hydrazones and vicinal dihydrazones has wide applications as a fundamental reaction in diazoalkane synthesis[2,3] using mercuric oxide as dominant oxidizing reagent. For example, while aromatic ketone hydrazones **1**[2,4] and **2**[5] are transformed into the corresponding diazo compounds, benzil monohydrazone **3** yields α-diazoketone[6~8] and dihydrazone **4** is converted into diphenylacetylene **12**.[9,10]

While $Th^{+}\cdot$ was reduced quantitatively to thianthrene (Th), the diazo compounds, diazodiphenylmethane **7**, 9-diazofluorene **8**, and phenylbenzoyl diazomethane **9** were produced in good yields by the oxidation of **1**, **2**, and **3**. Results are given in Table 1. The mechanism for the formation of $Ar_2C=N_2$ is shown in Scheme 1, although we do not have sufficient knowledge of the mechanistic details to establish the sequence of steps shown with $Th^{+}\cdot$ as oxidant. Route (a) in Scheme 1 is a net electron transfer reaction and deprotonation steps occuring by basic nitrile solvents. Route (b) shows that $Th^{+}\cdot$ bonds to the nitrogen atom of the hydrazone. We favor the second route since it is analogous to the reactions of $Th^{+}\cdot$ with aryl aldehyde oximes,[11] and with hydrazonitriles.[1] In those reactions, $Th^{+}\cdot$ bonds to the nitrogen atom of aldoxime produced aldehyde[11] and bonds to the nitrogen atom of hydrazonitrile produced an azo compound.[1] In route (b) on Scheme 1, the formation of the diazo compound may originate from intermediates **5** and **6** resulting from attack of $Th^{+}\cdot$ on the nitrogen atom of ketone hydrazone. Reactions between ammonia, or primary and secondary alkylamines, and the sulfur atom in $Th^{+}\cdot$ and analogous cation radicals have been reported and may serve as precedents for favoring the route (b) mechanism.[12,13]

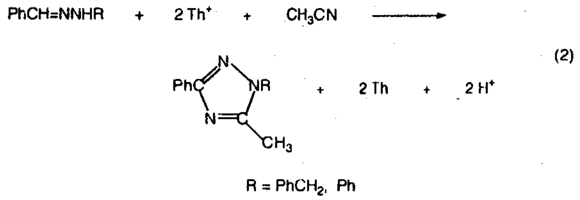
Bezophenone hydrazone **1** reacted rapidly with $Th^{+}\cdot ClO_4^-$



Scheme 1.

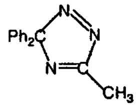
in acetonitrile to give the oxidation product **7** a 94% yield (run 1, Table 1).[14] To date, diazo compound **7** has only been prepared by oxidation of **1**. The method of oxidation reported here, insofar as this example is concerned, provides a good synthetic route to **7**, and raises the interesting consideration of the possibility of cation radical-induced oxidation.

Also, aromatic ketone hydrazones **2** and **3** yielded the expected oxidation products **8** and **9** in good yield. The carbonyl group in **3** was not vulnerable to the attack of the thianthrene cation radical. Generally, it has been reported that only ketones with an α-H atom react with cation radicals.[15]



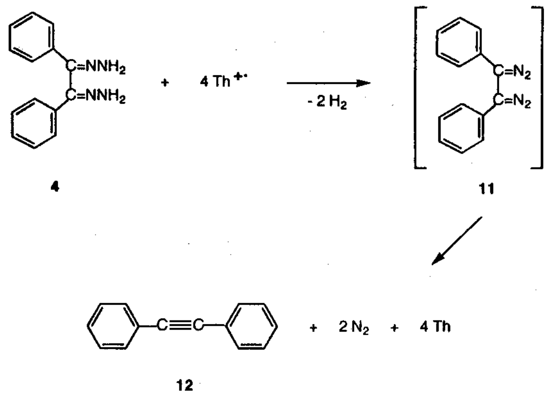
(2)

Studies of cation radical induced oxidative cycloaddition of arylhydrazones of benzaldehyde and butyraldehyde to nitriles (eq 2)[16] have stimulated our interest in the possibility that 3,3-diphenyl-5-methyl-1,2,4-triazole **10** can be found from the reaction of unsubstituted ketone hydrazones with $Th^{+\cdot}$ in acetonitrile solvent. However, no triazole **10** was obtained from any of the four ketone hydrazones in our study.



10

It is known that **10** has a theoretically unlikely structure and is unstable due to the steric strain caused by placing two phenyl groups on the same carbon.[17] It readily decomposes into diazo compound.



Scheme 2.

In contrast with the anticipated oxidations of **1**, **2**, and **3**, the oxidation of **4** yielded product **12** instead of the initially expected 1,2-bisdiazo-1,2-diphenylethane **11**. The mechanism was considered to be very similar to that depicted in Scheme 1 except that the nitrogen evolution and the mole ratio of $Th^{+\cdot}$ to **4** was 4 : 1 (Scheme 2). The oxidation of **4** by $Th^{+\cdot}$ did not produce the diazo compound **11** as its final product. But, there is no reason to doubt the intermediacy of **11**, even if no such compound has yet been isolated. Bisdiazoalkane is known as a potential intermediate in the synthesis of strained cyclic olefins, and becomes more and more stable the farther apart the diazo groups are.[17] Thus, **11** which has a vicinal bisdiazo group, will not survive long enough, and will yield **12** with an accompanying loss of nitrogen. However, this reaction would be useful for conducting an elegant synthesis of alkynes.

Thianthrene (Th) and thianthrene 5-oxide (ThO) were also obtained in each oxidation, as shown Table 1. Th is a major redox product, but the formation of ThO stems from the reaction of $Th^{+\cdot}$ with water which was present in the solvent or was added in workup.[18] This is evident, particularly, where a large excess of $Th^{+\cdot}$ was used.

In conclusion, the thianthrene cation radical can be used in place of the toxic, pollution-causing mercuric oxide as an oxidizing agent for the oxidation of aromatic ketone hydrazone. The new oxidation process described herein considerably broadens the scope for the oxidation of ketone hydrazones.

Acknowledgment. We would like to thank Chonnam National University for its generous financial assistance, and Dr. Sung Sin Choi, of the Kum Ho R & D Center for GC-MS.

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Preparation of Polyenes with an Allylsilane Moiety Using 2-(Phenylsulfonylmethyl)-3-(trimethylsilyl)propene and Their Cyclization Reactions

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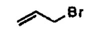
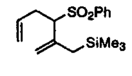
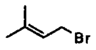
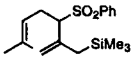
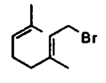
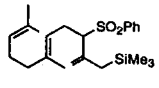
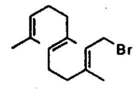
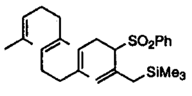
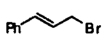
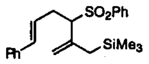
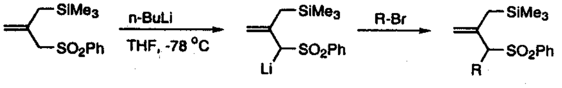
Lewis acid-induced intramolecular annulations of allylsilanes with an electrophilic terminus such as epoxide, aldehyde, ketone, enone, acetal, oxonium ion, and iminium ion were extensively applied for a regioselective formation of several ring systems.[1] However, the cyclization of allylsilane with simple alkene terminator is quite rare.[2] We describe herein the preparation of the polyenes with an allylsilane moiety **3** using 2-(phenylsulfonylmethyl)-3-(trimethylsilyl)propene (**1**) and their cyclizations to form methylenecycloalkanes. Compound **1** was readily prepared by the reaction of 2-(iodomethyl)-3-(trimethylsilyl)propene with sodium benzenesulfinate at 100 ℃ in N,N-dimethylformamide.[3] When the bifunctional reagent **1** was treated with *n*-butyllithium in THF at −78 ℃, α-lithiosulfone **2** was generated selectively and then treated with allylic bromides gave the correponding allylation products **3** in good yields (Table 1).

Table 1. Allylation of the bifuntional reagent **1**

Entry	Allylic bromide	Allylsilane **3**	Yield (%)
a			87
b			82
c			79
d			90
e			95

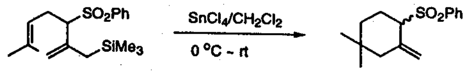
When the allylsilane **3b** was treated with stannic chloride (3 equivalents) in dichloromethane at 0 ℃ to room temperature, the methylenecyclohexane **4** was produced in 76% yield.[4] Due to complexation with the sulfone oxygens an excess of Lewis acid was required. The allylsilane cleanly cyclized to the cyclohexane having an exocyclic double bond. The regioselectivity in this reaction is controlled by the remarkable ability of silicon to stabilize a developing carbocation β to itself.[5] Stannic chloride appears to be the most promising Lewis acid for the cyclization of the allylsilanes **3**.



1 **2** **3**

In the ^1H NMR spectrum the two methyl protons of **4** appear at higher field (δ 0.82 and 1.02) than the methyl protons of **3b** (δ 1.54 and 1.62). This indicates that the methyl groups in **4** are bonded on sp^3 carbon atoms while the methyl groups in **3b** are attached to sp^2 carbon atoms.

On the contrary, the reactions of the allylsilanes **3a** and **3e** with Lewis acid afforded only desilylated products.



3b **4**

Cyclization of **3c** under the same reaction conditions gave 8-methylenedecaline **5** in 75% yield.[6] Surprisingly, this reaction occurred stereoselectively, and only **5a** was formed between two possible epimers. The chemical shifts of the three methyls at δ 0.70, 0.78, and 0.86 in the ^1H NMR spectrum indicates that the methyl groups are no longer attached to olefinic carbon atoms. The stereochemistry at the C-7 pheny-