tion of the carbanion in this way explains why the allylation reaction with allylic carbonates can be carried out without addition of bases. Nucleophilic attack of carbanion on π-allylpalladium gives the allylated product, with regeneration of Pd(0)-phosphine.

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A Novel Cation Radical Induced Oxidation of Hydrazonitriles

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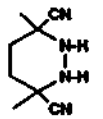
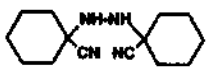
Much attention has been focused on the oxidation of hydrazonitriles [N,N'-dicyanoalkylhydrazines], which are among the most important intermediates for synthesizing azonitriles. Azonitriles are widely used as a source of radicals and biradicals.[1] In particular 1,1'-azobiscyclohexanecarbonitrile (ACN, 9) and 2,2'-azobis-1-isobutyronitrile (AIBN, **10**) are useful as polymerization initiators and blowing agents for thermoplastics.[2]

We now present an account of a new cation radical induced oxidation of one cyclic and two acyclic hydrazonitriles; namely 3,6-dicyano-3,6-dimethylpiperidazine (**1**), 1,2-di-1-(1-cyano)cyclohexylhydrazine (**2**), and 1,2-di-2-(2-cyano)propylhydrazine (**3**).



1



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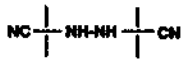


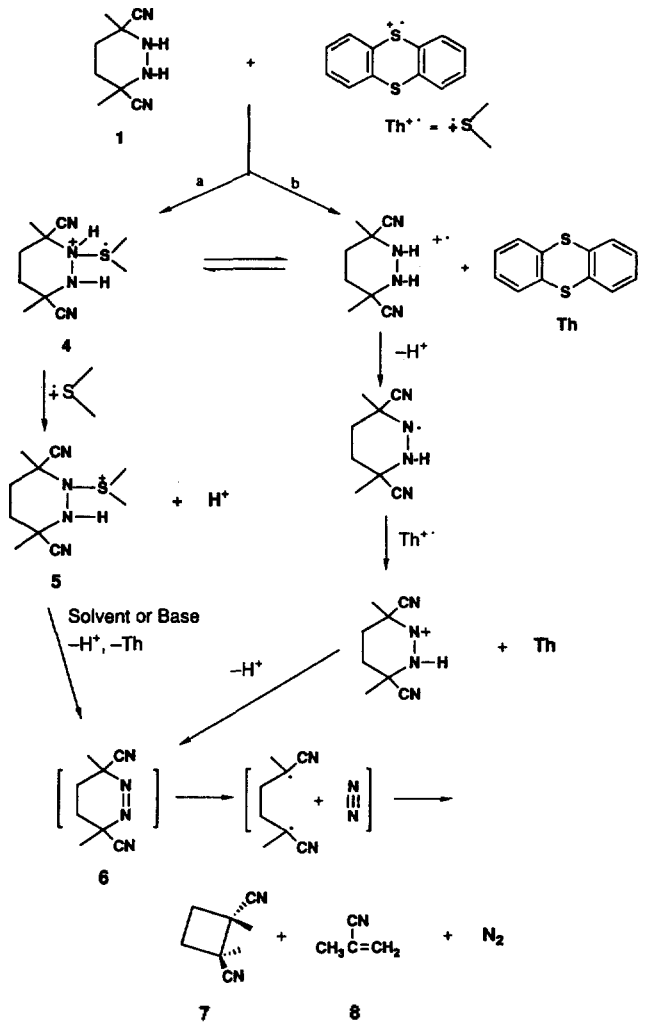
3

The reaction of **1** with thianthreniumyl perchlorate ($Th^{+\cdot}ClO_4^-$) was carried out in both the absence and presence of 2,6-di-tert-butyl-4-methylpyridine (DTBMP). The reaction took 1 day without DTBMP, but was completed within 5 minutes in the presence of DTBMP. Results are given in Table 1. Instead of the cyclic azoalkane, 3,6-dicyano-3,6-dimethyl-1,2-diazacyclohexene (**6**), the coupled product, trans-1,2-dicyano-1,2-dimethylcyclobutane (**7**) and the cleavage product, methacrylonitrile (**8**) were obtained with nitrogen evolution. There are two ways in which product formation can be visualized, although mechanistic detail for establishing the sequence of steps has not been validated. One of the possible routes is (a) in Scheme 1, which shows that $Th^{+\cdot}$ bonds at the nitrogen atom of **1** and that the intermediate (**4**) thus formed is oxidized by a second molecule of $Th^{+\cdot}$, giving intermediate **5**. The other [route (b)] is a net electron

Table 1. Products (%) of Reaction of Thianthrene Cation Radical with Hydrazonitriles in MeCN at Room Temperature[a]

Run	Hydrazonitrile[c]	Products (%)[b]					
		7	8	9	10	Th	ThO
1[c]	DCDMP	49	25			76	6
2[d]	DCDMP	49	26			95	3
3	DCCH			81		79	2
4	DCPH				92	92	3

[a] Oxidation was carried out by adding acetonitrile by syringe to a stirred, septum-capped round-bottomed flask containing the solids, 1.00 mmol of $Th^{+\cdot}ClO_4^-$ and 0.50 mmol of hydrazonitrile, under argon until the color of $Th^{+\cdot}$ was discharged. Stirring was continued for 24 h. Water was then added, the solution was neutralized with $NaHCO_3$ and extracted repeatedly with CH_2Cl_2. [b] Second entry in each run. Products were identified and quantified by GC, using the method of "standard addition" of authentic samples,[22] 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 °C at 10 deg/min. The hydrazonitriles and the four products were prepared by standard procedures as referenced and had satisfactory GC/ MS, NMR, and other data. [c] After 24 h stirring, the color of $Th^{+\cdot}$ was dispelled. [d] DTBMP (1.5 mmol) was placed in the flask with the $Th^{+\cdot}ClO_4^-$ and 1 before solvent was added (the mole ratio used was 3 : 2 : 1). The color of $Th^{+\cdot}$ was discharged completely within 5 minutes.



Scheme 1.

transfer reaction and deprotonation steps by basic nitrile solvents. Mechanistic route (a) can be understood in the light of the reaction of $Th^{+\cdot}$ with aldoximes.[3] In that work, complexation of aldoxime with $Th^{+\cdot}$ led to aldehyde formation. Route (a) like route (b) allows also for the formation of the hydrazonitrile cation radical and is analogous to the complexation mechanism that has been popularized for cation radical-nucleophile reactions by Parker.[4] In a complexation mechanism **4** would be a complex, rather than a covalently bound pair. It may well be that this is, in fact, the route to **5**.

Hydrazonitrile cation radicals have not been investigated previously except for conformationally protected hydrazine cation radicals such as bis-bicyclic and 2,3-dialkyl-2,3-diazabicyclo[2.2.2]octanes.[5] Hydrazonitrile cation radicals do not have long lifetime due to rapid deprotonation.

The effect of the added DTBMP in this reaction enhances the reaction rate of formation of abnormal oxidation products **7** and **8**. Therefore, it seems that the function of added DTBMP is to increase the rate of deprotonation, without which the second oxidation step by thianthrene cation radical would be slow.

The oxidation of the **1** by $Th^{+}ClO_4^{-}$ did not yield the cyclic *azo* compound as final product. It has been reported that **6** decomposes even at 0 ℃ to give the products **7** and **8** by oxidation with $KMnO_4$ in acetone and bromine in aqueous in alkali.[6] The cyclic cis azoalkane, **6** is labile due to steric strain caused by placing bulky groups on the same side (cis-configuration) of the *azo* linkage[7~9] and mutual repulsion of the lone pairs on nitrogen[10] in a six membered ring and decomposes readily by radical-stabilizing effect of the cyano groups at the α-carbon atoms.[11] UV spectroscopic evidence for the presence of the *azo* intermediates at −78 ℃ strongly supports the instability of the cyclic *azo* alkane at room temperature and the reaction proceeds *via* the unstable *azo* intermediate.[7] It is well known that the decomposition of *azo* compounds occurs by a free radical mechanism, with loss of nitrogen thermally or photochemically.[1,2,12~14] Also, in the present study, the cyclic *azo* compound **6** had to be decomposed *via* 1,4-biradical with rapid evolution of nitrogen to yield **7** and **8** directly. In the case of **7**, a pure trans isomer[15] was obtained by the coupling of an intermediate 1,4-biradical although the stereochemical configuration of **1** was not resolved.

Oxidation of **2** to **9** has been reported by others. For example, anodic oxidation gave **9** in 77% yield in NaCN-MeOH.[16] Oxidation by potassium ferricyanide gave **9** in 50-90% yield[17,18] and by bromine in 84-90% yield.[19]

In contrast with the oxidation of **1**, **2** gave the *azo* compound **9** in reaction with thianthrene cation radical. The azoalkane, **9** is known to be a more efficient radical initiator than **10** for generation of a radical.[20] The mechanism of this reaction would be similar to route (a) or route (b) in Scheme 1 except nitrogen evolution.

1,2-Di-2-(2-cyano)propylhydrazine (**3**) reacted rapidly with $Th^{+}ClO_4^{-}$ in acetonitrile to give oxidation product **10** in 92% yield (run 4, Table 1). The method of oxidation reported here, insofar as this example is concerned, provides a good synthetic route to **10**, and raise the interesting consideration of the possibility of cation radical induced oxidation. Also, this reaction can be understood with the former oxidation mechanistic scheme of **1**.

Thianthrene (Th) and thianthrene 5-oxide (ThO) were also obtained in each oxidation, as shown in 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.[21] This is evident, particulary, where a large excess of $Th^{+\cdot}$ was used. Product balances account for the average of about 74.2% of hydrazonitrile and 88.7% of the thianthrene cation radical.

The cation radical salt-induced oxidation of tertiary hydrazonitriles has been shown to produce the corresponding oxidation products, but an unstable azoalkane **6** decomposed to give the cleavage and coupling products with nitrogen evolution. The new reaction described herein further expands the scope of oxidation of hydrazonitriles.

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Iron Pentacarbonyl-Mediated Stereoselective Carbonylation of *trans*- and *cis*-Monobromocyclopropanes

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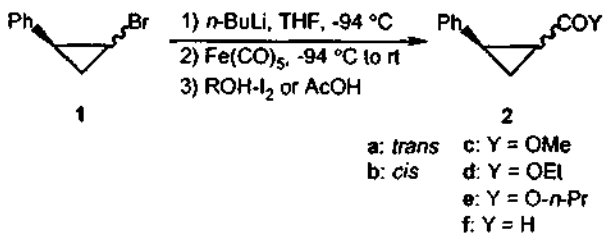
The cyclopropane moiety is present in a large number of natural products and pharmaceutically interesting compounds. *gem*-Dihalocyclopropanes which can be readily prepared from the addition reaction of dihalocarbene with olefins are one of the most versatile starting materials for the synthesis of the substituted cyclopropanes.[1] Reductive carbonylation of *gem*-dibromocyclopropanes is the most valuable method for the synthesis of cyclopropanecarboxylic acid derivatives. Although $Ni(CO)_4$,[2~4] $Fe(CO)_5$,[5] and $CoCl_2 \cdot 6H_2O$/Ni $(CN)_2 \cdot 4H_2O$[6] (phase transfer conditions, PTC) have been utilized for the conversion of the *gem*-dibromocyclopropanes to the cyclopropanecarboxylic acid derivatives, these did not afford desirable yield and stereoselectivity. On the other hand, we reported recently that tetracarbonylhydridoferrate, $HFe(CO)_4^-$, generated by the reaction of $Fe(CO)_5$ with alkaline medium worked as an efficient reducing agent for the mono-dehalogenation of *gem*-dihalocyclopropanes.[7] The isolation of its stereoisomers led us to look for the stereoselective synthesis of cyclopropanecarboxylic acid derivatives using the monobromocyclopropanes. Herein we report the $Fe(CO)_5$-mediated diastereoselective carbonylation of the *trans*- and *cis*-1-bromo-2-phenylcyclopropanes.



Scheme 1.

Results and Discussion

Although many transition metal salts have been utilized for the carbonylation of *gem*-dihalocyclopropanes to give the cyclopropanecarboxylic acid derivatives, the reactions using monohalocyclopropanes have been scarcely explored. Several attempts for the carbonylation reaction of the bromocyclopropane **1** were not successful under the reported systems.[2~6] However, halogen-lithium exchange was essential for the carbonylation of **1**. Treatment of *trans*-1-bromo-2-phenylcyclopropane (**1a**) (1 mmol) with *n*-BuLi (1.2 equiv) followed by successive addition of iron pentacarbonyl (1.2 equiv) in tetrahydrofuran at −94 ℃ and methanol-I_2 afforded *trans*-1-methoxycarbonyl-2-phenylcyclopropane (**2ac**) stereospecifically in 86% yield (Scheme 1). When the reaction using other alcohols such as ethyl and *n*-propyl alcohols was also applied to this carbonylation under the identical reaction conditions, the corresponding 1-alkoxycarbonyl-2-phenylcyclopropanes were obtained stereospecifically in high yields. When this lithiation-$Fe(CO)_5$-induced alkoxycarbonylation also proceeded with *cis*-1-bromo-2-phenylcyclopropane (**1b**) under the similar reaction conditions, the stereochemistry of the carbonylated cyclopropanes was always *cis*. The addition of acetic acid to the reaction mixture in place of alcohol-I_2 afforded the cyclopropanal stereospecifically, which was oxidized spontaneously to the cyclopropanecarboxylic acid under air. Typical results are summarized in Table 1. The multiplicities and coupling constants of the carbonylated cyclopropanes are shown in Experimental Section.

Plausible reaction pathway for the carbonylation of *trans*-