which the sign of α is negative. That is, not only the magnitude of the exchange constant alternates, but the sign also alternates along the chain from ferromagnetic to antiferromagnetic. We note that measurements such as these would not have been possible for a system with α of this magnitude but positive, for the low-temperature diamagnetism of the singlet ground state of the pair would preclude the observation of the antiferromagnetic interpair interaction. A molecule of this sort is copper acetate–pyrazine.[7,8]

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Oxidative Decomposition of 1,1'-Azoadamantane by Thianthrene Cation Radical. Carbocationic Chemistry from a Free Radical Source

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In the course of studies in the trapping of free radicals, we have discovered that azoalkanes are readily oxidized by aromatic cation radicals in acetonitrile at room temperature. The mechanism of this novel reaction is examined here for the particular case of thianthrenium perchlorate (Th$^+$·ClO$_4^-$) and 1,1'-azoadamantane
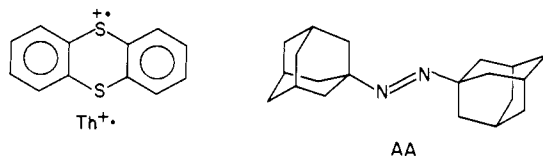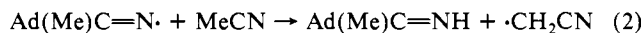

(AA). *trans*-AA undergoes conventional thermolysis into adamantyl radicals (Ad·) in solution at reasonable rates only if heated in the region 280–300 °C.[4,5] In contrast, reaction of this very stable azoalkane with Th$^+$· at room temperature leads to rapid
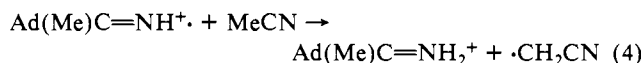
and quantitative evolution of nitrogen.[6] The major products (Table I) are characteristic of adamantyl cations (Ad$^+$) while the minor ones imply a small free radical component of the reaction. In other words, predominantly carbocationic chemistry is observed from an azoalkane, a traditional source of free radicals.[7]

While Th$^+$· was reduced quantitatively to thianthrene (Th), the major product from AA was *N*-adamantylacetamide, which was isolated in 90% yield as its perchloric acid salt (cf. Table I). Without doubt, this product arose from hydration, during workup, of a Ritter-type intermediate (AdN=$^+$CMe) from reaction of Ad$^+$ with solvent acetonitrile. The small amount of 1-adamantanol (0.6%) must have been formed also from Ad$^+$ by reaction with water either adventitiously in the solvent or added later. Together, these products show that 91% of the adamantyl groups appeared as the cation. Three other products containing the adamantyl group were obtained: adamantane (AdH), 0.2%, 1,1'-biadamantyl (AdAd), 2.5%, and 1-adamantyl methyl ketone, AdCOMe, 5.5%. Thus, we have accounted for 99% of the adamantyl groups in the AA.

The formation of AdCOMe and AdH but not of the other products was completely suppressed by inclusion of a small amount (0.020 M) of BrCCl$_3$ in the solvent. The concomitant appearance of 1-bromoadamantane suggests that adamantyl radicals which would normally have given AdH and AdCOMe were trapped by bromine atom abstraction from BrCCl$_3$.[8,9] The source of Ad-COMe was found to be the ketimine Ad(Me)C=NH. Ketimines are known to hydrolyze readily during isolation.[10] Addition of an authentic sample of Ad(Me)C=NH after reaction was complete resulted in its quantitative hydrolysis to AdCOMe on workup. On the other hand, an authentic sample of Ad(Me)C=NN=C-(Me)Ad survived the reaction and workup conditions; hence, AdCOMe is not derived from hydrolysis of this azine. The ketimine may arise from iminyl radicals which are known to abstract hydrogen atoms both intra- and intermolecularly[11–13] in competition with their dimerization.[11,14] Iminium cation radicals[12,13]

$$\text{Ad· + MeCN} \rightarrow \text{Ad(Me)C=N·} \qquad (1)$$

$$\text{Ad(Me)C=N· + MeCN} \rightarrow \text{Ad(Me)C=NH + ·CH}_2\text{CN} \quad (2)$$

are better hydrogen abstracting agents, however (eq 3 and 4), and

$$\text{Ad(Me)C=N· + H}^+ \rightarrow \text{Ad(Me)C=NH}^+· \qquad (3)$$

$$\text{Ad(Me)C=NH}^+· + \text{MeCN} \rightarrow$$
$$\text{Ad(Me)C=NH}_2^+ + ·\text{CH}_2\text{CN} \quad (4)$$

these are more viable intermediates in our system. The necessary protons could easily derive from hydrolysis of some of the thianthrenium perchlorate[15–17] by the small amount of adventitious water in the solvent.

UV irradiation of AA in hydrocarbon solvents at 65 °C produces Ad· which mostly dimerizes to AdAd or abstracts hydrogen to give AdH.[5] Since these products are very minor in the present work, it appears that either Th$^+$· oxidizes Ad· with great facility

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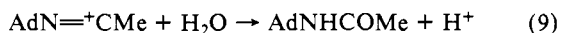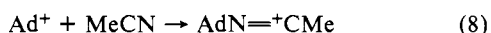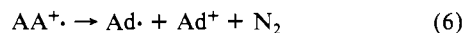(17) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

Table I. Products of Reaction of Thianthrene Cation Radical Perchlorate with 1,1'-Azoadamantane in Acetonitrile[a]

reactants[b]		products[b]						
AA	Th⁺·ClO₄⁻	AdNHCOMe[c]	AdOH[d]	AdCOMe[d]	AdH[d]	AdAd[c]	Th[c,h]	N₂[c,i]
0.459	0.815	0.752				0.011	0.822	
0.566	1.00	1.02[e]	0.0034	0.031[f]	0.001[g]	0.014		
0.051	0.050							0.0367
0.051	0.050							0.0398
0.027	0.0505							0.0273

[a] Distilled over P_2O_5. [b] In mmol. [c] Isolated yield. [d] GC assay, SE-30 capillary column, with naphthalene as an internal standard. [e] Isolated as the perchloric acid salt, amounting to 90% of the AA. The difference between this and the first entry (amounting to 81.9% of AA) represents losses in the extractive isolation of AdNHCOMe. [f] This represents 5.5% of the AA. Measurements in two other separate experiments gave 5.7% and 5.9% of the AA. [g] This represents 0.2% of the AA. [h] A small amount of thianthrene 5-oxide (ThO) was also obtained. [i] N_2 was measured by conventional vacuum-line. Toepler-pump techniques. In these cases, solid Th⁺·ClO₄⁻ and AA were placed in separate arms of a Y-tube, to each of which approximately 1 mL of acetonitrile was added. Reactants were mixed after customary freeze–thaw degassing and sealing.

or that very few free Ad· are formed. Such free Ad· that are produced mainly add to the nitrile carbon[18] rather than abstracting hydrogen from MeCN. In support of the possibly facile oxidation of Ad·, it should be noted that the ionization potential (IP) of Th is near 7.90 eV,[19,20] while the IP of Ad· should be similar to the 6.9 eV found for *tert*-butyl radical.[21] Moreover, Th has a higher oxidation potential (1.3 V) than Fe(phen)₃(ClO₄)₃ (0.99 V) but even the latter oxidizes *tert*-butyl radical rapidly.[9,22]

The simplest representation of the reaction of Th⁺· with AA and the formation of so much AdNHCOMe is given in eq 5–9.

$$Th^+\cdot + AA \rightleftharpoons Th + AA^+\cdot \qquad (5)$$

$$AA^+\cdot \rightarrow Ad\cdot + Ad^+ + N_2 \qquad (6)$$

$$Th^+\cdot + Ad\cdot \rightarrow Th + Ad^+ \qquad (7)$$

$$Ad^+ + MeCN \rightarrow AdN{=}^+CMe \qquad (8)$$

$$AdN{=}^+CMe + H_2O \rightarrow AdNHCOMe + H^+ \qquad (9)$$

Azoalkane radical cations (eq 5 and 6) have not been investigated previously except for a recent photochemical study of bicyclic azoalkanes in CCl_4.[24] Although many azoalkanes exhibit a molecular ion in mass spectrometry,[25] the irreversible nature of their cyclic voltammograms[26] is consistent with the postulated decomposition of AA⁺·. If eq 5–9 were the sole reaction pathways, the stoichiometry of reaction would be 2.00:1.00 Th⁺·/AA. However, in each of seven measurements of the ratio of reactants, made by adding AA until the color of the Th⁺· disappeared, we obtained a molar ratio of 2.00:1.13 Th⁺·/AA. This ratio can be accommodated by the escape of adamantyl radicals from oxidation (eq 7) and their entering into some other reactions. In that case, more AA would be needed for electron transfer to remaining Th⁺· than required by reactions 5–7 and the ratio 2.00:1.00. The ratio found, 2.00:1.13, says that 88.5% of adamantyl groups were oxidized to Ad⁺, which corresponds well with the 91% yield of Ad⁺-derived products.

Although the major products are rationalized by eq 1–9, the origin of the 2.5% biadamantyl remains uncertain. One would not expect free Ad· to recombine because reaction with solvent is far more probable; moreover, AdAd continued to form in the

presence of $BrCCl_3$. These considerations suggest that two Ad· are occasionally released in the same solvent cage, perhaps by decomposition of a complex of Th⁺· and AA. In that case, Th⁺· is regenerated and thus serves as a catalyst for the decomposition of AA into AdAd. Complexes of Th⁺· with nucleophiles have been identified kinetically by Parker and co-workers, e.g., with anisole.[27] The oxidation of AA by Th⁺· may involve such a complexation route.

In summary, a thermally stable azoalkane has been shown to undergo facile oxidative decomposition under mild conditions. The postulated intermediate, an azoalkane radical cation, has received scant attention previously, though the corresponding radical anions are known.[28] The new reaction described herein further expands the chemistry of the remarkably versatile azo linkage.[29,30]

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Novel Cycloaddition of Dimethylacetylene to the Dimethylacetylene Radical Cation: Direct Observation by ESR

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It has been well established that, for some aromatic and olefinic hydrocarbons,[1] the monomer radical cation reacts with the parent molecule to form the dimer cation with a sandwich structure. In contrast, we find a [1 + 2] cycloaddition of dimethylacetylene (DMA) radical cation to the parent molecule in solid Freon matrix at ca. 100 K. As far as we are aware, this is the first study in

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