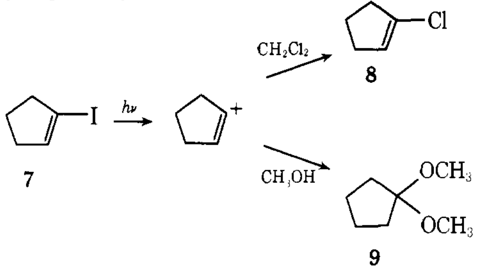
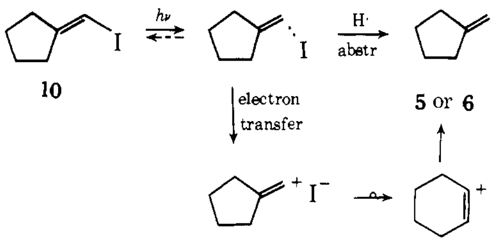
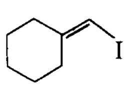
pentene (**7**) in methylene chloride at 40° afforded cyclopentene as the only detectable photoproduct (80%). However, at −25° the ionic product 1-chlorocyclopentene (**8**) was formed (18% yield) in addition. Similarly, irradiation in methanol at −25° afforded the ionic product 1,1-dimethoxycyclopentane (**9**, 13% yield). These are the first unequivocal examples of generation of the 1-cyclopentenyl cation.[8]



Irradiation of vinyl iodides has also afforded the first unequivocal route to the difficultly accessible primary vinyl cations.[9] Thus, for example, irradiation of (iodomethylene) cyclopentane (**10**) in methylene chloride or ethylene glycol afforded the ionic products **5** (23%) or **6** (30%), respectively, accompanied by the reduction product methylenecyclopentane (50%). Similar behavior was exhibited by the cyclohexyl analogue **11**, which afforded the chloride **12** and the ketal **13** (27%), along with reduced material.





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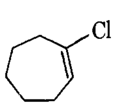

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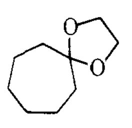
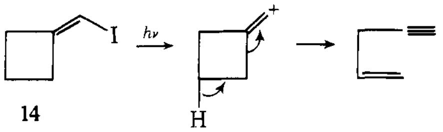


13

It is significant that the ionic products are ring expanded; apparently the cyclic cation, being secondary, is more stable despite the fact that it is constrained to be nonlinear. In an interesting contrast, the cyclobutyl analogue **14** principally underwent fragmentation to 1-penten-4-yne (60%) on irradiation in methylene chloride. In this case ring scission is more facile than isomerization to the secondary but highly strained 1-cyclopentenyl cation.



Thus photolysis of vinyl halides has afforded a number of vinyl cations not previously accessible. Further studies are in progress to elucidate the behavior of other vinyl cations prepared in this way.

Acknowledgements. Support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References and Notes

(1) For part 2 see G. A. Poindexter and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7142 (1974).

(2) P. J. Kropp, T. H. Jones, and G. S. Poindexter, *J. Am. Chem. Soc.*, **95**, 5420 (1973).

(3) Irradiations were conducted at 254 nm using a Rayonet RPR-100 reactor and quartz tubes containing 0.5 mmol of iodide dissolved in 10 ml of solvent. Where indicated, mossy zinc was employed as an iodine scavenger.

(4) Radical abstraction from methylene chloride occurs at hydrogen whereas cationic abstraction occurs at chlorine; see, K. V. Scherer, Jr., and R. S. Lunt, III, *J. Am. Chem. Soc.*, **88**, 2860 (1966), and E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd; *ibid.*, **95**, 8107 (1973).

(5) The origin of the effect of temperature on the ratio of ionic to radical products is not clear at this time. It does not appear to be due principally to the increased viscosity of the medium at lower temperatures since vinyl iodides show no significant increase in yield of ionic products on going to highly viscous solvents such as ethylene glycol. Saturated alkyl halides, which exhibit increased ionic behavior in more viscous solvents,[1] do not exhibit a similar temperature effect.

(6) C. Roberge and J. A. Herman, *Can. J. Chem.*, **42**, 2262, (1964); R. C. Neuman, Jr., *J. Org. Chem.*, **31**, 1852 (1966); R. C. Neuman, Jr., and G. D. Holmes, *ibid.*, **33**, 4317 (1968); and R. M. Wilson and T. J. Commons, *ibid.*, **40**, 2891 (1975).

(7) See P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973), and references cited therein.

(8) Solvolysis of 1-cyclopentenyl triflate and nonaflate have been reported; see W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Am. Chem. Soc.*, **93**, 1513 (1971), and L. R. Subramanian and M. Hanack, *Chem. Ber.*, **105**, 1465 (1972). However, it is not clear in these cases why reaction does not simply involve nucleophilic attack at sulfur rather than ionization to the cyclopentenyl cation.

(9) Except for (halomethylene)cyclopropanes, which gain special stabilization from the cyclopropyl group, primary vinyl cations have not been generated solvolytically.[6] Although several primary vinyl cations have been proposed as possible intermediates from decomposition of diazonium ions, alternative mechanisms involving unsaturated carbenes or other intermediates are suspect; see M. S. Newman and A. Kutner, *J. Am. Chem. Soc.*, 73, 4199 (1951); M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956); M. S. Newman and C. D. Beard, *ibid.*, **91**, 5677 (1969); M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969); M. S. Newman and C. D. Beard, *J. Am. Chem. Soc.*, **92**, 7564 (1970); and D. Y. Curtin, J. A. Kampmeier, and R. O'Connor, *ibid.*, **87**, 863 (1965).

(10) Alfred P. Sloan Research Fellow.

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Thermolysis and Photochemistry of Cyclic Azo Compounds. A Novel Chemiluminescent Reaction and Alternate Route to Dewar Benzene

Sir:

The thermal,[1] direct photochemical,[2] and triplet sensitized decomposition[3] reactions of cyclic azo compounds are believed to yield hydrocarbons via diradical intermediates. These thermal and photochemical eliminations of nitrogen are considered to be general reactions of cyclic azo compounds.[4] However, there are a number of perplexing examples in which the loss of nitrogen failed.[5]

Understanding why the cyclic azo compounds studied unexpectedly resisted loss of nitrogen is important if nitrogen elimination reactions are to be employed rationally in organic synthesis. We report a study of the thermolysis, direct photolysis, and triplet sensitized photolysis of the tetracyclic azo compound **1**[4] which (a) has demonstrated that fluorescence characteristics may serve as a guide to when a cyclic azo compound will lose nitrogen with difficulty; (b) has uncovered a novel chemiluminescent reaction; (c) has resulted in the development of an alternate synthesis of Dewar benzene; (d) has revealed the first example of a cyclic azo compound to undergo cleavage of different bond types when excited to its singlet (C–N bond cleavage) and triplet (C–C bond cleavage) states; and (e) has provided direct evidence for oxygen assisted intersystem crossing.

Thermolysis of **1** in *n*-dodecane results in quantitative formation[6] of benzene and nitrogen (eq 1). The activation parameters for thermolysis (temperature range 130–150°) are $\Delta H^{\ddagger} = 35.6$ kcal/mol and $\Delta S^{\ddagger} = 7.8$ eu. The closeness of these values to those reported[7] ($\Delta H^{\ddagger} = 36.7$ kcal/mol, $\Delta S^{\ddagger} = 8.7$ eu) for 2,3-diazabicyclo[2.2.1]hept-2-ene, **2**, is consistent with the rate determining step being similar, presumably involving cleavage of a C–N bond.

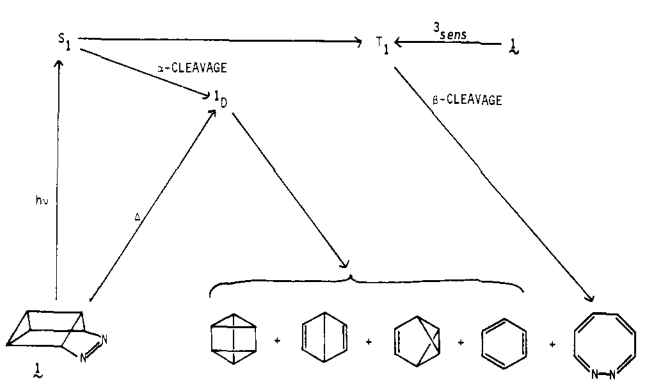
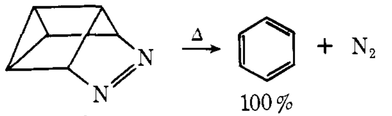
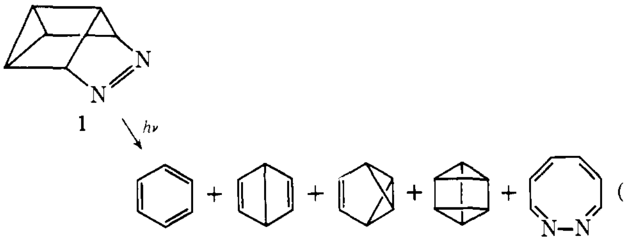


Figure 1. Scheme for the thermolysis (Δ), direct photolysis ($h\nu$), and triplet sensitized photolysis (^{3}sens) of **1**. ^{1}D represents a diradical produced from initial C-N bond cleavage.



1 100% (1)

Unlike the thermal chemistry, the photochemistries of **1** and **2** contrast strongly. The latter compound loses nitrogen with an efficiency approaching 1.0 for both direct photochemical and triplet sensitized excitation. Neither the direct nor triplet sensitized photolysis of **1** occurs with unit efficiency (quantum yields for disappearance of **1** being 0.6 and 0.3 for direct and sensitized photolysis, respectively). Indeed, **1** is weakly fluorescent ($\phi_F = 0.06$, $\tau_F = 50$ ns, 3-methylpentane, 20-25°), so that a direct probe of the deactivation of S_1 is available. At 25°, direct photolysis of **1** (excitation 366 nm) in deuterated cyclohexane results in formation[8,9] of benzene, Dewar benzene (**3**),[8b] benzvalene (**4**), prismane (**5**), and 1,2-diazacyclooctatetraene (**6**). *The product ratio was found to be markedly dependent upon the oxygen content of the sample (eq 2).*

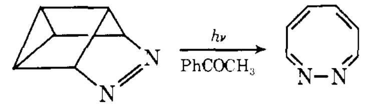


(2)

		3	4	5	6
oxygen	30%	30%	3%	7%	30%
nitrogen	30%	45%	6%	11%	8%

These observations may be the result of two pathways by which S_1 of **1** deactivates. One is an intrinsic pathway that is temperature independent (intersystem crossing) and the other is temperature dependent (C-N cleavage). At low temperatures, the C-N cleavage from S_1, requiring thermal activation, is inhibited and intersystem crossing from S_1 to T_1 dominates. This premise accounts for the previously reported photochemistry[8a] of **1** if **6** is formed exclusively from T_1.

In striking confirmation of this expectation we find that sensitization of the decomposition of **1** by acetophenone results in formation of **6** as the predominant product,[10] eq 3. Moreover, the variation of products in the direct photolysis of **1** (eq 2) may now be understood to result from oxygen assisted $S_1 \rightarrow T_1$ conversion.[11] At high concentration of oxygen, this process causes substantial increase in the yield of triplets and the yield of **6** is enhanced at the expense of the $(CH)_6$ isomers.



1 **6**, 67% (3)

Consider the mechanistic scheme shown in Figure 1 as a basis for interpreting the results of eq 1, 2, and 3. In the scheme ^{1}D is a diradical produced by exciting **1**, and S_1 and T_1 are the singlet and triplet excited states of **1**. The absence of benzene valence isomers among the products when T_1 is selectively produced by triplet sensitization, means that **3**, **4**, *and* **5** *derive only from* S_1. If thermolysis of **1** produces a species similar[12] to ^{1}D produced from S_1, then **3** should be a major product of the thermolysis.[13] However, as **3** is thermally unstable ($\Delta H^{\ddagger} = 25$ kcal/mol, $\Delta S^{\ddagger} = 1$ eu),[8b] it can only be a transient intermediate. Nevertheless, **3** in minute concentrations can be detected by its chemiluminescence as the thermolysis of **3** is known to produce benzene triplet.[14] Indeed, heating **1** with 9,10-dibromoanthracene (DBA) produces chemiluminescence identified as fluorescence of DBA, and the chemiluminescence yield indicates that the formation of **3** is the major source of chemiexcitation.[15] Since comparable solutions of neither benzvalene nor prismane chemiluminesce under the reaction conditions *we conclude that* **3** *is the major thermolysis product of* **1**. This reaction is, incidentally, a rare example of a chemiluminescent reaction that does not involve cleavage of an O-O bond or an oxidation.

In summary, oxygen assisted intersystem crossing and the competition between the rates of photophysical (fluorescence and intersystem crossing) and photochemical (C-N bond cleavage) deactivation of S_1 cause the photochemistry of **1** to be extremely temperature dependent. It is the energy barrier separating S_1 from ^{1}D which controls whether nitrogen is lost or not.

The fluorescence characteristics of azo compounds may, therefore, serve as a guide to whether nitrogen will be lost and at what temperature.[16] It is interesting to note that while C-N bond cleavage is the major chemical process undergone by S_1, C-C bond cleavage is the major process undergone by T_1. There is no precedent in the chemistry of cyclic azo compounds for this contrast.[17]

Acknowledgments. The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589), the National Science Foundation (Grants NSF-MPS70-02165 and NSF-MPS73-04672), and the National Institutes of Health (Grant GM-19173) for generous support of this work. The authors also wish to thank Dr. K.-C. Liu for measurements of the effect of temperature on the fluorescence of **1**.

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(1) C. H. Bamford and C. F. H. Tipper, Ed., "Comprehensive Chemical Kinetics", vol. 6, Elsevier, New York, N.Y., 1972, p 566.

(2) P. S. Engel and C. Steel, *Acc. Chem. Res.*, **6**, 275 (1973).

(3) For a comprehensive review of the photochemistry of azo compounds see *Spec. Period. Rep.: Photochem.*, **6**, and earlier volumes in this series.

(4) Carbon-carbon bond formation is expected to result from elimination of N_2 from cyclic structures. For example, see T. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973), and references 7-14 quoted therein.

(5) For example see ref 6 and J. A. Berson and R. F. Davis, *J. Am. Chem. Soc.*, **94**, 3658 (1972); D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel, *ibid.*, **93**, 3817 (1971); J. Synder, Ph.D. dissertation, Cornell University, 1967; W. L. Mock, Ph.D. dissertation, Harvard University, 1965.

(6) B. M. Trost and R. M. Cory, *J. Am. Chem. Soc.*, **93**, 5573 (1971).

(7) S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

(8) (a) Previously it has been reported that, at −78°, benzene and **6**[6] are the major products of direct photolysis of **1** and that at temperatures somewhat above room temperature **5** is formed in low yield.[4] (b) Because Dewar benzene does not form at low temperatures,[8a] and because it decomposes[8c] rapidly ($t_{1/2} < 1$ h) above 50°, there is an optimum temperature at which it can be prepared by photolysis of **1**. The yield of Dewar benzene is substantial. Dewar benzene elutes more rapidly than the other products upon GLC (5% didecyl phthalate plus triethanolamine),[8d] and it is therefore easy to prepare from **1**. Previously, Dewar benzene was available only by van Tamelen's classic procedure.[8e] (c) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Am. Chem. Soc.*, **94**, 5906 (1972); (d) H. R. Ward and J. S. Wishnok, *ibid.*, **90**, 1085 (1968); J. Kaplan and K. E. Wilzbach, *ibid.*, **89**,

1030 (1967); (e) E. E. van Tamelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963); E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971); E. E. van Tamelen and D. Carty, *ibid.*, **93**, 6102 (1971).

(9) The secondary conversion of **6** to benzene causes a variation in the observed ratio of benzene to **6** after extended photolysis. However, it appears that most of the benzene in the direct photolysis of **1** derives from S_1.

(10) Compound **1** quenches acetophenone phosphorescence at the diffusional rate in acetonitrile ($k_q = 8 \times 10^9$ M^{-1} s^{-1}). At less than 10% conversion, $\phi = 0.3$ for the photosensitized decomposition of **1**. Benzene is also formed (33%), but, as in the direct photolysis,[9] may arise from photosensitized decomposition of **6**.

(11) The possibility of oxygen assisted $S_1 \rightarrow T_1$ conversion has been suggested previously, but not established definitely: W. D. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971); G. L. Loper and F. Dorer, *ibid.*, **95**, 20 (1973).

(12) That this might be the case has precedent in the literature: P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968).

(13) The intermediacy of **3** in the thermolysis of **1** was previously considered as a possibility, but rejected because of the absence of **3** as product when **1** is pyrolyzed in the vapor phase.[6]

(14) Dewar benzene and its simple derivatives are generally chemiluminescent: P. Lechtken, R. C. D. Breslow, A. H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973).

(15) A quantitative comparison of the chemiluminescence yield from **1** and **3** indicates that if **3** is formed it must be produced in high yield in order to account for the observed chemiluminescence intensity. That **3** is formed is corroborated by the observation that the ratio of indirect chemiluminescence from DBA and 9,10-diphenylanthracene is identical when **3** or **1** is the source of chemiexcitation. That benzene triplet is the chemiexcited species involved is corroborated by the observation that the Stern-Volmer constant for the quenching of chemiluminescence by *cis*-butene is the same as for the quenching of benzene triplet by *cis*-butene.

(16) The competition between fluorescence and intersystem crossing in cyclic azo compounds varies widely with structure, Dr. K.-C. Liu, Columbia University, unpublished results. Indeed, some [2.2.2]diazabicyclooctenes possess fluorescence yields approaching unity. Clearly, nitrogen cleavage will be efficient only at temperatures at which the activation barrier to C–N cleavage in S_1 is overcome.

(17) An intriguing possibility is that the contrasting behavior of S_1 and T_1 may be due to an *adiabatic* photoreaction of T_1 to some triplet of **6** or its precursor. This possibility is presently under investigation.

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Received March 1, 1976

Redox Properties of Copper-Thiaether Complexes. Comparison to Blue Copper Protein Behavior

Sir:

The unique spectral and redox properties of blue copper proteins have been the subject of much interest, particularly since, until recently, they eluded duplication by model complexes.[1,2] In a recent communication[3] we reported the first examples of low molecular weight Cu(II) complexes, involving a series of cyclic and open-chain polythiaethers, which exhibit an intense absorption band in the 600-nm region, the hallmark of the blue copper proteins. Ancillary crystallographic structural studies[4] and single crystal spectra[5] indicate that this characteristic absorption band results from a thiaether sulfur-to-copper charge transfer band *which is not dependent on coordinative distortion* as had been previously suggested.[6,7]

Markedly positive Cu(II)-Cu(I) formal electrode potentials (+0.2 to +0.8 V vs. SHE at pH ~7) have also been a recognized characteristic of the blue copper proteins, the source of which has long been in controversy.[8,9] Ligands which sterically or electronically destabilize tetragonal Cu(II) and/or enhance the stabilization of Cu(I) can shift the formal Cu(II)-Cu(I) reduction potential to more positive values.[10] Many workers have suggested that either tetrahedral or trigonal bipyramidal coordination is implied by the high redox potentials (and spectral properties) of the blue copper proteins.[6,7] In pursuing this hypothesis, Patterson and Holm recently examined a broad series of Cu(II) complexes to identify specific ligand structural features which might give rise to Cu(II)-Cu(I) potentials in the blue copper protein range.[11] However, most of the 37 complexes examined by them exhibited negative potentials with respect to SHE.

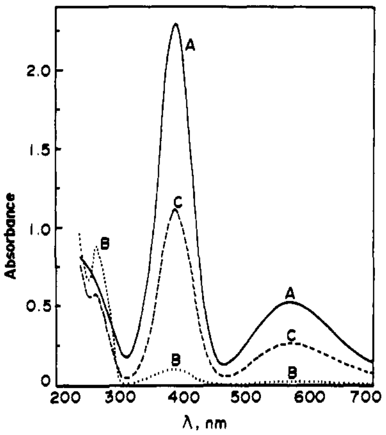

Figure 1. Absorbance spectra (1-cm cell) of a solution containing 5.68×10^{-4} M total copper ion and 5.59×10^{-4} M total 14-ane-S_4 ligand (L) in a matrix of 0.1 M $HClO_4$ in 80% methanol–20% water (by weight). Curve A represents the initial solution: [Cu(II)L] = 2.69×10^{-4} M, [Cu(II)] = 2.99×10^{-4} M, [L] = 2.90×10^{-4} M. Curve B represents the same solution after 85% reduction by electrolysis at 0.45 V (vs. SHE); [Cu(I)L] = 4.75×10^{-4} M, [Cu(II)L] = 1.25×10^{-5} M, [Cu(II)] = 8.0×10^{-5} M, [L] = 7.1×10^{-5} M. (Note the Cu(I) peak at 265 nm.) Curve C represents the reduced solution after exposure to air for 1 week showing partial reoxidation. Curve A is completely regenerated either by continued exposure to air or by oxidative electrolysis.

We wish to report at this time the results of a systematic investigation on the redox properties of a series of Cu(II)-polythiaether and polyaminothiaether complexes which exhibit redox potentials in the blue copper protein range *independent of coordinative geometric constraints.* The ligands studied include the seven cyclic and one open-chain species for which the spectral properties of the Cu(II) complexes were previously reported[3] plus eight closely related species (Table I). All ligands were synthesized and purified by established procedures[12] or modifications thereof. Due to the sparing solubility of the 12 polythiaether compounds in water, all redox measurements were carried out in 80% CH_3OH–20% H_2O (by weight), corresponding to the conditions utilized for our previous spectral[3] and kinetic[13] studies on these systems.

For each of the Cu(II) complexes studied, $E_{1/2}$ values were estimated from cyclic voltammetric measurements (platinum electrode system) in which cathodic and anodic peaks were identified for the process:

$$Cu^{II}L + e^- = Cu^{I}L$$

where L represents the coordinated polythiaether or polyaminothiaether ligand. To confirm the nature of the redox process involved, Cu^{II}(14-ane-S_4) was completely reduced by controlled potential coulometry at +0.45 V (vs. SHE) requiring 1.00 ± 0.02 electrons per equivalent of complex. The reduced solution yielded cyclic voltammetric behavior which was virtually identical with that of the original solution ($E_{1/2} = 679 \pm 10$ mV). This Cu(I) solution exhibited no visible spectrum but showed an absorption peak in the ultraviolet region (Figure 1, curve B). That this peak is characteristic of Cu(I) was confirmed by measuring the spectrum of an aqueous solution (deaerated) of CuCl in 0.1 M $HClO_4$. Reoxidation of the Cu^{I}(14-ane-S_4) solution at +0.95 V (vs. SHE) regenerated the original spectrum (see Figure 1) indicating that the ligand structure was not disrupted by the electrolysis. The reduced complex was found to be stable over a period of several weeks under N_2 atmosphere but when exposed to air is slowly reoxidized to Cu^{II}(14-ane-S_4) (see Figure 1).

As shown in Table I, all of the $E_{1/2}$ values for the polythiaether complexes S_3 to S_6 are in the range of +0.67 to 0.90 V (vs. SHE) among the highest values reported for the