Computer subtraction of the spectrum of **4b** isolates the spectrum of the second major reaction product (Figure 1, bottom). We assign its structure as **1** on the basis of the following evidence: (i) the relative intensities of peaks in the IR spectrum remain the same in a series of experiments under varying conditions, indicating that only one species is involved; (ii) the IR spectrum remains unchanged when the matrix is annealed at 45 K for 3 h,[20] indicating that none of the major peaks belong to radicals;[21] (iii) the use of cesium in argon[22] at 115 °C in place of potassium and the use of 1,4-dibromobicyclo[2.2.1]heptane (**4d**)[23] at 150 °C in place of the diiodo precursor **4a** still lead to spectra containing the bands assigned to **1** and **4b**, although the degree of conversion is lower, demonstrating that neither the metal nor the halogen are present in the molecule;[24] (iv) the spectrum is compatible with the structure and quite similar to that of **3**, with characteristic cyclopropane CH$_2$ stretches at 3056 and 2997 cm^{-1} (3065 and 2989 cm^{-1} in **3**), CH$_2$ bends at 1445, 1439, and 1430 cm^{-1} (1454 and 1438 cm^{-1} in **3**), and intense peaks at 1044 and 906 cm^{-1} (1030 and 955 cm^{-1} in **3**) in regions characteristic for cyclopropanes and cyclobutanes, respectively;[25] both spectra exhibit a very intense peak at low frequencies (**1**, 530 cm^{-1}, **3**, 515 cm^{-1}); (v) heavy doping of the matrix with bromine during the course of the deposition,[26] isolation of warmup products by pumping into a trap and working up rapidly with pentane and aqueous bisulfite, followed by comparison of GC retention times and mass spectra (EI and CI), show the presence of 12% **4b**, 11% **5**, and 77% **4d** as the only major products.[27,28]

The importance of ultrasound mixing to the success of the experiments should be noted. Without sonication, higher reaction temperatures were necessary and the reaction was still incomplete. The trapping with bromine then produced 12% **4a**, 52% **4c**, 23% **4d**, and 8% 1-bromobicyclo[2.2.1]heptane (**4e**) as the major products.

The very high intensity of the peak at 530 cm^{-1}, located in a region characteristic for skeletal deformation vibrations, which are usually of negligible intensity, is quite striking and may reflect an unusual charge distribution in small-ring propellanes.

All attempts to isolate or chemically trap **1** by distilling the matrix into a cold vessel met with failure. We hypothesize that **1** oligomerizes or polymerizes with extreme ease. This is perhaps not surprising in view of the expected extreme weakness of the central bond. Taking 27 and 28 kcal/mol as the strain energy of cyclobutane and cyclopropane, respectively, 17 kcal/mol as the strain energy of norbornane, and an estimate of 10 kcal/mol for the bridgehead distortion energy of **1**, one finds that approximately 75 kcal/mol of strain energy is relieved in breaking the bridgehead–bridgehead bond. Even if the bridgehead distortion energy were zero and the strength of a C–C bond were taken as 85 kcal/mol, the energy of this bond can be no more than 20 kcal/mol. This indicates that **1**, along with [2.2.2]propellane,[8,29] may contain the most highly strained C–C bond yet synthesized. A more detailed discussion of this point is not warranted at this time, but it is interesting to note that barring a dramatic increase in the bridgehead distortion energy, the bridgehead–bridgehead bonds of both [2.1.1]- and [1.1.1]propellanes will actually be stronger than that in [2.2.1]propellane due to the larger residual strain left in the resultant biradical.

Further investigations of **1** and of the reaction of 1,4-diiodobicyclo[2.1.1]hexane with alkali metal vapors are currently under way.

Acknowledgment. We express our gratitude to Professor D. H. Aue for stimulating discussions and to A. D. Otteson, who contributed much to the development of the reactor system. Support for this project was provided by NSF grants CHE 78-27094 and CHE 78-24880.

Registry No. 1, 36120-90-8; **4a**, 40950-21-8; **4b**, 279-23-2; **4c**, 930-80-3; **4d**, 40950-22-9; **4e**, 13474-70-9; **5**, 18313-42-3; **6**, 59219-48-6.

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[18] Babad, H.; Flemon, W.; Wood, J. B., III *J. Org. Chem.* **1967**, *32*, 2871.

[19] In the pyrolysis of [3.2.1]propellane, D. H. Aue and collaborators detected small amounts of 4-methylenecycloheptene in addition to 1,3-dimethylenecyclohexane (personal communication).

[20] The optical quality of the matrix deteriorates in the process such that small peaks are no longer visible.

[21] Attempts to anneal to higher temperatures resulted in a loss of the matrix.

[22] The spectrum also contains **6** and large amounts of **4a**.

[23] The spectrum also contains **4e** and **6**, as well as large amounts of **4d**.

[24] Reaction of **4a** with sodium vapor required temperatures of 190 °C and gave only **4b** and **6**.

[25] Bellamy, L. J. "The Vibrational Spectra of Complex Molecules"; Chapman and Hall: London, 1975; Vol. I, pp 18, 32, 33; Vol II, pp 8, 18.

[26] Sublimed at −78 °C through a tube held ~1 cm from the cold window.

[27] Control experiments gave complete recovery of starting material in the absence of metal vapor. Bromine will react with **4a** under more vigorous conditions. In CH$_2$Cl$_2$ at 41 °C with excess Br$_2$ the rate constant is 1.8 × 10^{-4} s^{-1}. In less polar solvents such as C$_6$H$_{12}$, no reaction occurs even at 80 °C: Pratt, W. E., Ph.D. Thesis, Yale University, New Haven, Conn., 1978.

[28] Controls showed that substantial amounts (about 70%) of **4b** are lost in workup. Also, some of **1** is sprayed onto the radiation shield and other parts of the cryostat, preventing its reaction with bromine, and we have no means of measuring the efficiency of reaction of bromine with **1**. These factors undoubtedly exaggerate the amount of **5** obtained. Percentages are corrected for detector response factors.

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Triplet ESR Spectrum of the Copper Porphyrin Cation Radical

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It is well recognized that metalloporphyrin cation radicals play a key role as reaction intermediates in photosynthetic and metabolic processes.[1] They are also an interesting group of compounds insofar as metal ion is surrounded by a conjugated π radical. For these reasons, they have been attracting the increasing attention of chemists in diverse fields. Cation radicals with different central metal ions have been generated chemically, electrochemically, and photochemically, and their electronic structures have been extensively investigated by optical absorption and ESR spectroscopy.[2-5] The central metal ions studied so far are mostly diamagnetic. It is expected that ESR spectra of the cation radicals with paramagnetic metal ions, if observed, will provide valuable information about the electronic structure of the systems. Copper porphyrin cation radicals belong to such species. They are the systems with one odd electron on the central metal ion and the other on the porphyrin ring. Therefore, their spin state is either singlet or triplet depending on which is lower in energy. No triplet ESR spectrum, however, has been detected for any of them. This has been speculated as being due to a singlet ground state or to line broadening of triplet spectra.

We report the first detection of a triplet ESR spectrum of a copper porphyrin cation radical produced in tetrachloroethane matrix at 77 K by γ radiolysis. Figure 1 shows the X-band ESR spectra at 77 K of a degassed tetrachloroethane solution of 10^{-3} M copper octaethylporphyrin (Cu$^{\mathrm{II}}$OEP) before and after γ irradiation. The solution was irradiated with a 3.2 Mrd dose of γ rays from a ^{60}Co source. Since little information was available in the region around $g = 2$ owing to the strong signal of solvent radicals, the spectra taken with high gain are presented showing clear signals in the other region. The irradiated sample shows a pair of signals on both sides of the solvent radical signal with

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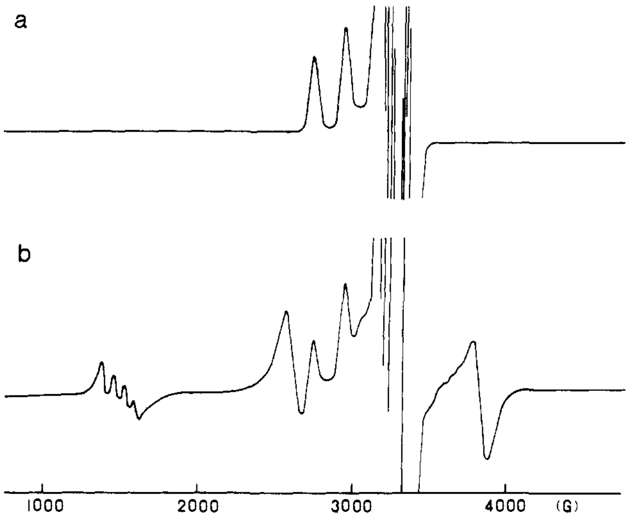
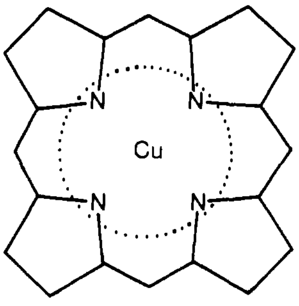


Figure 1. X-band ESR spectra of $Cu^{II}OEP$ in tetrachloroethane at 77 K: (a) before γ irradiation; (b) after γ irradiation.

a separation of 1210 G and a four-line signal centered at about 1430 G, as shown in Figure 1b. No such signals were detected under the same experimental conditions in the absence of the solute. These new signals are characteristic of triplet species, that is, the paired signals at high field are ascribed to the $\Delta ms = 1$ transitions and the signal at low field to the $\Delta ms = 2$ transition. The observation of only a pair of signals at high field suggests that the triplet species has near or complete axial symmetry, and these paired signals, each of which shows asymmetric line shape, can be regarded as the perpendicular component of the fine structure, that is, the value of 1210 G corresponds to the fine structure constant, *D*. Furthermore, the value of 2.049 is obtained as the perpendicular component of the g tensor from the midpoint between the pairs of lines. This value is very close to that of the perpendicular component of the g tensor of $Cu^{II}OEP$.[6] The *D* value can also be derived from the position of the $\Delta ms = 2$ transition.[7] The calculated value is 0.1181 cm^{-1}, whereas the value obtained from the $\Delta ms = 1$ transitions is 0.1158 cm^{-1} (1210 G is converted by using $g = 2.049$). The very good agreement between the two values confirms that the preceding assignment of the observed spectrum to a triplet species and the analysis of the fine structure are correct. The splitting of the $\Delta ms = 2$ transition into four lines with an average separation of 75 G can be ascribed to the hyperfine structure due to one copper nucleus ($I = {}^3/_2$). This value for the copper hyperfine coupling constant implies that the unpaired spin density on the copper atom is fairly large. All the above considerations lead to the assignment of the observed triplet spectrum to $[Cu^{II}OEP]^{+\cdot}$, the cation radical of $Cu^{II}OEP$.

It has been well established that one-electron oxidation of solute molecules takes place by radiolysis of alkylhalide solutions.[8-10] This technique has been successfully applied to the formation of cation radicals of chlorophylls[11,12] and metal porphyrins.[13,14] The oxidation is caused through electron abstraction from solute molecules by solvent cation radicals produced by ionizing radiation. When radiolysis is performed at 77 K, oxidation products are usually stabilized due to the rigidity of the solvent matrices. In the present case, the optical absorption spectrum of the irradiated sample gives additional evidence for the formation of $[Cu^{II}OEP]^{+\cdot}$. The visible absorption spectrum of the irradiated solution at 77 K shows a decrease in absorption intensity of $Cu^{II}OEP$ with the appearance of a broad absorption at longer wavelengths. The new absorption is similar to that reported for $[Cu^{II}OEP]^{+\cdot}$ generated in dichloromethane electrochemically.[4] When the irradiated solution at 77 K is warmed to room temperature, the broad absorption at longer wavelengths disappears and the solution gives no triplet ESR spectrum upon being recooled to 77 K. This may be due to the disappearance of $[Cu^{II}OEP]^{+\cdot}$ by reactions with radiation-induced products of the solvent molecules.

We now proceed to interpret the observed triplet spectrum more quantitatively by using a simple model. In $[Cu^{II}OEP]^{+\cdot}$, one odd electron localizes in the $3d_{x^2-y^2}$ orbital of the copper atom located at the center of the porphyrin plane, while the other is delocalized in the highest occupied π orbital of the porphyrin ring as a first approximation. The two orbitals have no region of space in which they are simultaneously nonzero, and as a consequence the exchange integral between them is nil. Therefore a possible mechanism for exchange interaction is superexchange through the in-plane σ bonding between the copper atom and the pyrrole nitrogens. Its magnitude, however, is unlikely to be so large as to make a significant contribution to *D*. On the basis of this consideration, we assume that the observed *D* arises mostly from the electron–electron magnetic dipole interaction. For the dipole calculation, we simplify the above picture as a system with one odd electron distributed uniformly on a circle of radius *r*, and the other localized at the center of the circle in the *xy* plane. It is straightforward to calculate the dipolar-splitting tensor for this model.[15-17] The three components of the diagonalized tensor are $X = Y = -g^2\beta_2/4r^3$ and $Z = +g^2\beta^2/2r^3$. The fine structure constant, $|D|$, is given by ${}^1/_2(x - y) - z = 3g^3\beta^3/4r^3$. One obtains $r = 2.3$ Å by using $g = 2.0$ and $|D| = 1210$ G. The result is illustrated in I, in which the circle of $r = 2.3$ Å centered at the copper atom in the porphyrin plane is depicted by the dotted line.



I

As to the hyperfine splitting due to the copper atom, it has been reported that the triplet spectra of copper porphyrin dimers, which have one odd electron in each $3d_{x^2-y^2}$ orbital of the two copper atoms in close proximity, exhibit the seven-line hyperfine structure with a separation of 90–100 G for the $\Delta ms = 2$ transition,[18,19] this splitting constant is close to that observed for $[Cu^{II}OEP]^{+\cdot}$. This fact is in accord with the above described model, in which only one odd electron residing on the copper atom is responsible for the hyperfine splitting. Thus, the present model, though oversimplified, can give a reasonable account of the observed triplet spectrum of $[Cu^{II}OEP]^{+\cdot}$.

It remains to be solved as to why $[Cu^{II}OEP]^{+\cdot}$ prepared electrochemically showed no triplet ESR spectrum. The problem

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should be clarified by careful comparison of it with Cu^{II}OEP oxidized by different methods.

Further investigations with other copper porphyrins and copper chlorophyll are under way. The detailed results and discussions will be presented in a full paper.

Registry No. Cu^{II}OEP, 14409-63-3; [Cu^{II}OEP]$^{+\cdot}$, 74891-14-8.

An Unusually Facile Thioallylic Rearrangement: Stereochemical Evidence for a Free-Radical Chain Mechanism

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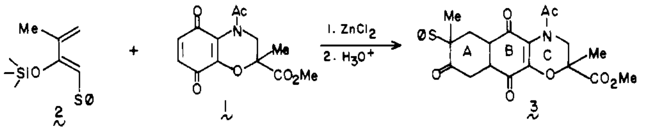
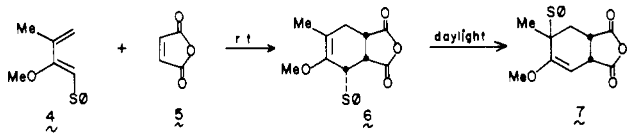
In the course of our efforts to synthesize the rubradirin antibiotics,[1] we had the occasion to study the Diels–Alder reaction of 2-alkoxy-1-phenylthio-1,3-butadienes with various dienophiles. We noticed that when the quinone **1** was reacted with 3-methyl-1-(phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadiene (**2**)[2] in the presence of zinc chloride, a facile rearrangement of sulfur apparently took place during the Diels–Alder reaction as evidenced by the appearance of the A-ring methyl group as a singlet in the ^{1}H NMR spectrum of the hydrolyzed product.[3]



To provide confirmatory evidence for this notion, we decided to investigate the reaction of the simpler dienophile maleic anhydride with 2-methoxy-3-methyl-1-phenylthio-1,3-butadiene (**4**).

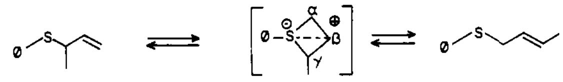


These materials reacted rapidly at room temperature to deliver the expected cycloadduct **6** in nearly quantitative yield provided the reaction flask was properly concealed from light (the flask was simply wrapped with aluminum foil). When a deuterochloroform solution of the crystalline cycloadduct (mp 95.5–96.5 °C) was allowed to stand for 1.5–2 days exposed to the laboratory lighting or ordinary daylight (an NMR tube of the sample was simply taped to the window!), a remarkably facile and essentially quantitative rearrangement took place. The same transformation could be effected thermally, but in poorer yield, by refluxing a toluene solution of **6** in the dark for several hours. The new product was clearly that of a 1,3 thio shift, for an olefinic proton was now visible at δ 4.78 (d, $J = 3.6$ Hz), and the methyl group appeared as a sharp singlet at higher field strength (δ 1.37). (In **6** the methyl group appeared as a broad singlet at δ 1.71.) Additionally, the doublet that appeared at δ 4.27 ($J = 5.8$ Hz) in the 300-MHz ^{1}H NMR spectrum of the starting material, which is ascribable to the proton on the carbon bearing the phenylthio substituent, was now absent.

The cycloadduct derived from *N*-phenylmaleimide and 3-methyl-1-(phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadiene was also observed to undergo ready thioallylic rearrangement under similar conditions. Here, however, hydrolysis of the enol silyl ether was observed to occur concurrently with the 1,3 sulfur shift, thus complicating the isolation.[4]

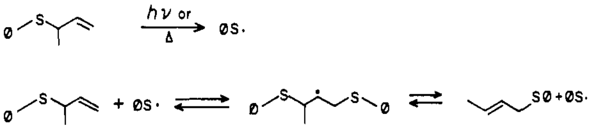
While thioallylic rearrangements are themselves certainly not uncommon, we felt that our particular example provided an excellent opportunity to investigate the stereochemical consequences of this process. To our knowledge, most thioallylic rearrangements have been studied previously in acyclic systems with no attempt having been made to ascertain their precise stereochemical characteristics.[5]

Two different proposals have been put forth regarding the mechanism of the thioallylic rearrangement reaction. Kwart has provided *conclusive* evidence for an associative mechanism when the substituent on sulfur is an electronegative phenyl group in which an intermediate is generated with the sulfur atom assuming a hypervalent state through electron donation from the allylic double bond to create a trigonal-bipyramidal (TBP or equivalent) structure (see eq 1).[6] Secondary deuterium isotope effects appear to indicate some degree of bonding between the central β-carbon atom and sulfur. Kwart has moreover suggested that "the photocatalyzed isomerization travels a path which is parallel to that of the thermal reaction".[7]



(1)

Other workers have argued that the thioallylic rearrangement reaction (both thermal and photochemical) occurs by a radical chain mechanism. The heat or light initiates the reaction by bringing about cleavage of the allyl–sulfur bond. In the next step, the phenylthio radical so produced adds to the double bond of the allyl sulfide, leading to a new radical which now loses the resident phenylthio group to generate the rearranged isomer.[5] Krusic and Kochi have, in fact, detected by ESR spectroscopy the presence of the symmetrical radical formed when dimethyl disulfide is photolyzed in the presence of allyl methyl sulfide.[8] While such a radical pathway is accessible to alkyl allyl and allyl aryl sulfides, the failure of alkyl allyl sulfides to undergo thermal thioallylic isomerization is in keeping with Kwart's proposed TBP configuration for the thioallylic intermediate (aryl is needed to stabilize the TBP).[6a] The associative mechanism does thus appear to be quite well established for the rearrangement of allyl phenyl sulfides (see eq 2).



(2)

[§] Camille and Henry Dreyfus Teacher–Scholar.

[†] Dupont Experimental Station, Wilmington, Delaware.

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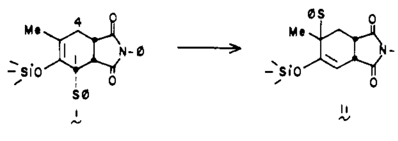

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