of tetraphenylhemin or other simple hemins destroys the parent compound, 1-Fe^{III}Cl is completely stable in the presence of 2-Fe, and the redox cycle can be carried out repeatedly without hemin destruction. This makes this type of hemin particularly attractive for catalytic oxidation or dioxygen reduction.

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE81-20969, for support of this research.

Registry No. 1-P, 74684-36-9; 1-Fe^{III}Cl, 86767-72-8; 1-Zn, 82925-38-0; 2-P, 82934-47-2; 2-Fe(1-MeIm)$_2$, 86784-90-9; 2-Zn, 86767-73-9; FeSO$_4$, 7720-78-7; Zn(OAc)$_2$, 557-34-6; *m*-CPBA, 937-14-4; Hm$^+$, 16009-13-5; 1-MeIm, 616-47-7; S$_2$O$_4$$^{2-}$, 14844-07-6; SnCl$_2$, 7772-99-8; *p*-cresol, 106-44-5.

Thioxyallyl Ion from Allene Episulfide with Acid

Wataru Ando,* Yukio Hanyu, Toshiya Furuhata, and Toshikazu Takata

Department of Chemistry, University of Tsukuba
Sakuramura, Ibaraki 305, Japan

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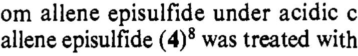
Interest has quickened over the last few years to claim the tautomeric system of cyclopropanethione–thioxyallyl ion–allene episulfide[1] in connection with analogous oxygen system.[2,3] De Boer[4] and Block[1] showed that under drastic conditions, thermodynamically stable allen episulfide (**1**) was produced presumably from cyclopropanethione (**3**) formed in situ, via thioxyallyl ion (**2**). Such an inference would be reasonable at first glance, but a closer look reveals that no definitive evidence either for thioxyallyl ion (**2**) or cyclopropanethione (**3**) is shown.[5]



1 2 3

Meanwhile, chemistry associated with the cyclopropanone–oxyallyl ion–allene oxide tautomeric system has been extensively studied,[2] and even oxyallyl ion has been widely used as a versatile synthetic reagent.[6]

We have presumed that thioxyallyl ion (**2**) can serve as an intermediate in the allene episulfide–cyclopropanethione tautomerism and now present direct evidence for the formation of thioxyallyl ion from allene episulfide under acidic conditions.[7]

Tetramethylallene episulfide (**4**)[8] was treated with fluorosulfonic acid (FSO$_3$H) as a solvent in NMR sample tube, cooling with liquid nitrogen in glovebox. The separated solid mixture was co-warmed gradually to −70 °C to mix, affording a light yellow solution. In the ^{1}H NMR spectrum of the solution, only a singlet signal at 3.09 ppm appeared besides an acid proton (FSO$_3$H) and was assigned to four equal methyl groups of the protonated thioxyallyl ion **5**. The ^{13}C NMR chemical shifts were observed at 248.3(s), 137.8(s), and 38.4(q) ppm, which were certainly in accordance with the existence of large positive charge at carbons of **5** (Figure 1).[10] **5** shows no appreciable decomposition at −60 °C but by warming to room temperature the solution changed to dark brown and no well-identified carbonium ion was found in the NMR spectra due to the instability of the thioxyallyl ion.

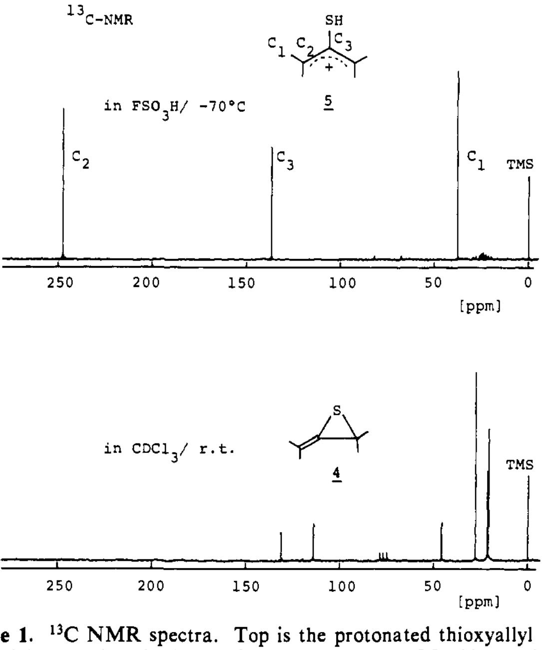


Figure 1. ^{13}C NMR spectra. Top is the protonated thioxyallyl ion **5** formed by treating **4** with FSO$_3$H as a solvent. Me$_4$Si sealed with CD$_2$Cl$_2$ in a capillary was held at the center of the NMR sample tube. Bottom is **4** in CDCl$_3$ with internal Me$_4$Si.

By treating **4** with slightly weaker acids such as HClO$_4$ as a Brønsted acid and BF$_3$ etherate as a Lewis acid under mild conditions, a few interesting dimerization products were obtained in good yields.[11]

4 (1.6 mmol) reacted with excess BF$_3$ etherate (4.8 mmol) or 70% perchloric acid (HClO$_4$, 0.6 mL)[12] in ether to give in a few minutes thioketone **6** and 1,4-dithiane **7**,[13] whereas in CH$_2$Cl$_2$, 1,3-dithiolane **8** as well as **6** and **7** were obtained (eq 1).[14] The structures of these products were fully determined by elemental analyses and spectroscopic data.[15] The light red color of **6** is well associated with the very low ^{13}C NMR chemical shift (276.2 ppm) assigned for the thioketone carbon. The quartet signal of the isopropyl methyl groups in the ^{1}H NMR spectrum of **8** is clearly consistent with a structure in which the isopropyl group is attached to an asymmetric carbon.

The formation of these products is well explained by assuming the thioxyallyl ion **9** as a reactive intermediate that possibly

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(1) Block, E.; Penn, R. E.; Ennis, M. D.; Owens, T. A.; Yu, S.-L. *J. Am. Chem. Soc.* **1978**, *100*, 7436–7437.

(2) (a) Chan, T. H.; Ong, B. S. *Tetrahedron* **1980**, *36*, 2269–2289. (b) Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25–32.

(3) Block et al. reported that allene episulfide (**1**) is 7 kcal/mol more stable than cyclopropanethione (**3**).[1] This situation is reverse for the cyclopropanone–allene oxide system.[2]

(4) Longejan, E.; Buys, Th. S. V.; Steinberg, H.; De Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 214–218.

(5) Recently, Saalfrank et al. postulated the intermediacy of thioxyallyl ion in the reaction of elemental sulfur with substituted allene produced in situ by thermolysis of oxaphosphetane. However, they did not isolate either allene episulfide or cyclopropanthione: Saalfrank, R. W.; Paul, W.; Schierling, P.; Schüler, H.; Wilhelm, E. *Chem. Ber.* **1982**, *115*, 57–64.

(6) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61–66.

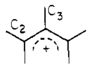
(7) Ring-opening reaction of thiiranes with C–S bond cleavage by acid is known to proceed via an opened cationic species by kinetic study: Odden, A.; Wylde, J. *Bull. Soc. Chim. Fr.* **1967**, 1607–1612.

(8) Tetramethylallene episulfide (**4**) was prepared by bulk vacuum pyrolysis of the lithium salt of tosylhydrazone of tetramethyl-3-thietanone, as reported by Hortmann et al.[9]

(9) Hortmann, A. G.; Bhattacharjya, A. *J. Chem. Soc.* **1976**, *98*, 7081–7082.

(10) These shifts are approximately consistent with those for allyl cations by Olah et al. i: ^{1}H NMR 2.91 ppm (CH$_3$). ((a) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 938–943). ii: ^{13}C NMR C$_2$: 234.7 (s) and C$_3$: 142.7 (s). ((b) Olah, G. A.; Bollinger, J. M. *Ibid.* **1968**, *90*, 6082–6091).

i



ii

(11) The yields of the products in acid-catalyzed dimerization of **4** were exceptionally high and no polymer was observed. Generally, yields of dimers from other thiiranes are low enough due to the formation of much polymer (e.g., 15% of dimer for styrene sulfide[12]).

(12) Noshay, A.; Price, C. C. *J. Polymer Sci.* **1961**, *54*, 533–541.

(13) The formation of dimer **7** has been reported by Hortmann et al. in the reaction of **4** with HClO$_4$; however, physical and spectroscopic data and even the yield were not given.[9]

(14) All yields are those isolated by column chromatography.

(15) Supplementary material available.

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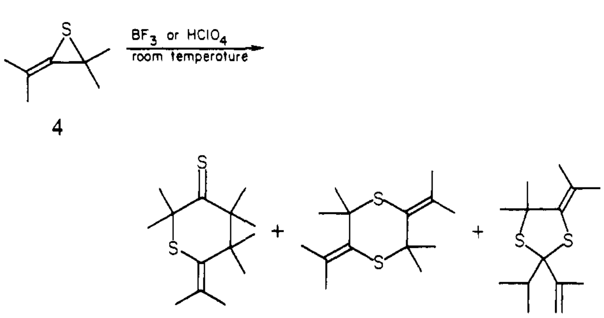
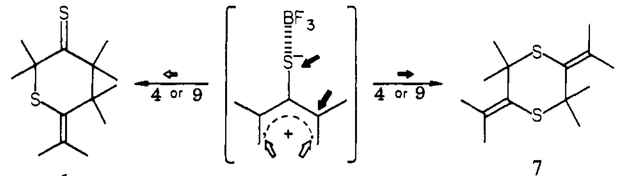


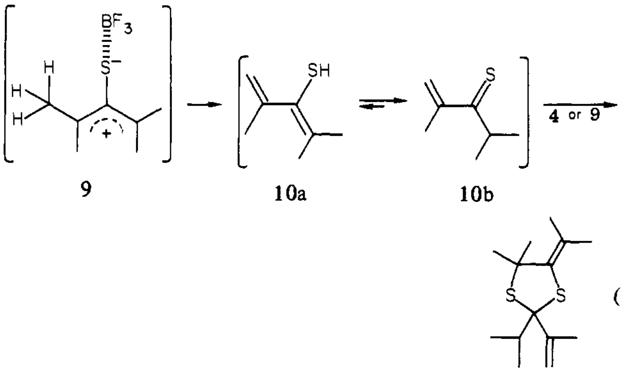
solvent	acid	6	7	8
ether	BF$_3$	11%	76%	0%
	HClO$_4$	6%	78%	8%
CH$_2$Cl$_2$	BF$_3$	trace	64%	13%
	HClO$_4$	trace	23%	44%

undergoes cycloadditions with either **4** or **9** to give **6** and **7** in ether (eq 2).



6 9 7

On the other hand, the thioxyallyl ion **9** might be expected to undergo 1,4-H shift, which would lead directly to the product **8** via **10** in CH$_2$Cl$_2$ (eq 3).[16] Similar rearrangement has been reported by Turro et al. in the thermal reaction of 2,2-dimethylcyclopropanone.[17]



9 10a 10b 8

The effect of solvent is important in determining the behavior of the thioxyallyl ion. More polar solvent gives slow rearrangement, and here less polar solvent permits more rearrangement. The yield of **8** indeed increased, in response to decrease of ether and increase of CH$_2$Cl$_2$ as solvents.[18] Similar solvent effect has been reported in an allene oxide rearrangement.[19]

Work is now in progress on the reactions with thioxyallyl ion with several electrophiles and the synthetic application of it.[20]

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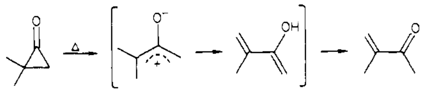
(16) The proton shift (eq 3) should be intramolecular rather than intermolecular because there is no appropriate base, and five-membered transition state favors Ei reaction. Intramolecular ethyl group shift may be fit for Saalfrank's.[5]

(17) Turro et al. obtained isopropenyl methyl ketone in an attempt to



collect cyclopropanone by preparative GC: Hammond, W. B., Turro, N. J. *J. Am. Chem. Soc.* **1966**, *88*, 2880–2881.

(18) The yield of **8** in the HClO$_4$/CH$_2$Cl$_2$ system is quite high since there is "no" ether (small amount of ether is always present in BF$_3$ etherate/CH$_2$Cl$_2$ system).

(19) Grimaldi, J.; Malacria, M.; Bertrand, M. *Tetrahedron Lett.* 1974, 275–277.

Registry No. 4, 61097-65-2; **5**, 86748-24-5; **6**, 86766-00-9; **7**, 86748-25-6; **8**, 86748-26-7; **9**, 86765-99-3; FSO$_3$H, 7789-21-1; BF$_3$ etherate, 109-63-7; HClO$_4$, 7601-90-3.

Supplementary Material Available: ^{1}H and ^{13}C NMR, infrared, and mass spectral and elemental analytical data and physical constants for the compounds **6**, **7**, and **8** (1 page). Ordering information is given on any current masthead page.

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(20) In the presence of the acetone and chalcone, treatment of the allene episulfide with BF$_3$ etherate readily gave the cycloadducts of the additives as well as small amount of the dimers. The adducts strongly (but not completely) reveal the formation of the 1,3-dipolar thioxyallyl ion **9** as an actual reactive intermediate. The detail results are to be published elsewhere after more work.

Electron-Transfer Catalysis by Surfactant Vesicle Stabilized Colloidal Platinum

Kazue Kurihara and Janos H. Fendler*

Department of Chemistry
and Institute of Colloid and Surface Science
Clarkson College of Technology
Potsdam, New York 13676

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This communication reports the formation of stable platinum colloids in the interior of polymerized surfactant vesicles and their use in the hydrogen gas mediated reduction of extravesicular compounds via vesicle embedded electron and/or hydrogen carriers (Figure 1).

Surfactant vesicles were prepared by cosonicating dipalmitoylphosphatidylcholine (DPPC), either with a styrene-containing surfactant [H$_2$C=CHC$_6$H$_4$NHCO(CH$_2$)$_{10}$](C$_{16}$H$_{33}$)N(CH$_3$)$_2$N$^+$Br$^-$ (**1**)[1] or [CH$_2$=CH(CH$_2$)$_8$CO-O]$_2$NPO(OH)$_2$ (**2**)[1] for 10 min at 60 °C and 150 W.[2] Platinum ions were entrapped in the mixed DPPC/**1** or DPPC/**2** vesicles by the addition of solid K$_2$PtC$_4$ and further sonication.[2] Vesicle-entrapped ions were separated from those in the bulk and/or attached to the outer surface by gel filtration and passages through an anion exchange resin.[3] Irradiation of Ar-bubbled K$_2$PtCl$_4$-containing vesicles by a 450-W xenon lamp at room temperature for 30 min resulted in the formation of colloidal platinum and the concomittant polymerization of **1** or **2** in the matrices of DPPC/**1** or DPPC/**2** vesicles. Colloid formation and polymerization were monitored absorption spectrophotometrically.[1,4] Importantly, no appreciable K$_2$PtCl$_4$ could be entrapped in vesicles prepared exclusively from DPPC. Furthermore, DPPC vesicles underwent time-dependent spontaneous fusion, which, ultimately, lead to their precipitation.[7]

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(1) Preparation, purification, and characterization of **1** are given in: Tundo, P; Kippenberger, D. J.; Klahn, P. L.; Prieto, N. E.; Jao, T. C.; Fendler, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 456–461.

(2) Typically, 10–20 mg of DPPC + 5–10 mg of **1** or **2** were dispersed in 5.0 mL of water at 60 °C for 10 min under an Ar atmosphere by means of a Bransonic 1510 ultrasonifier set at 150 W. Following the addition of 1–5 mg of solid K$_2$PtCl$_4$, the DPPC/**1** or DPPC/**2** vesicles were sonicated for an additional 10 min at 60 °C and 150 W. The purity of DPPC (Sigma) was established by thin-layer chromatography.

(3) Gel filtration was carried out on a 15 × 250 mm Sephadex G-50 column and a 11 × 250 mm BioRad AG 1-X2 50–100 mesh column was used for anion exchange.

(4) Irradiation of 4.7 × 10^{-4} M aqueous neutral K$_2$PtCl$_4$ solution by a 450-W xenon lamp (using only water as filter) led to the appearance of a broad band in the visible region and to a decrease of absorbance below 250 nm due to colloidal platinum formation possibly by PtC$_4^{2-}$ $\xrightarrow{h\nu}$ PtCl$_3^-$ + Cl$^-$,2PtCl$_3^-$ → Pt + PtCl$_4^{2-}$ + Cl$_2$.[5] Photoreduction of K$_2$PtCl$_4$ is enhanced in the presence of reductants, such as alcohols used in thermal reductions.[6]

(5) Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 2574–2579.

(6) Hirai, H. *J. Macromol. Sci. Chem.* **1979**, *A13*, 633–649. Hirai, H.; Nakao, Y.; Toshima, N. *Ibid.* **1979**, *A13*, 727–750.

0002-7863/83/1505-6152$01.50/0