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Photochemical Activation of Zinc-Carbon and Zinc-Sulfur Bonds in Zinc Porphyrins

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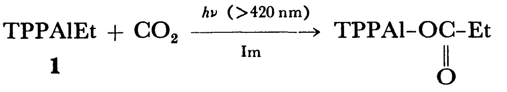
Ethyl(*N*-methyltetraphenylporphinato)zinc (NMTPPZnEt **2**) reacts with thiol (RSH: R=Pr^n, Bu^t, Ph) and hydrogen sulfide (H_2S) to form *N*-methyltetraphenylporphinatozinc sulfide (NMTPPZnSR: R=Pr^n, Bu^t, Ph, H). Irradiation with visible light enhances the reactivity of **2** in the reaction with Bu^tSH and brings about the homolytic cleavage of the zinc-sulfur bond of NMTPPZnSPr^n in dichloromethane.

The photochemistry of metalloporphyrins is of current interest in connection with the conversion of solar energy into chemical energy.[1-3] We have been studying the photochemical behavior of metalloporphyrins of aluminium and zinc which have an axial ligand bound to the metal *via* a σ-bond, and have found some very interesting effects of visible light on the reactivity of the axial ligand of the metalloporphyrins.

Ethyl(tetraphenylporphinato)aluminium (TPPAlEt **1**), which is unreactive to carbon dioxide in the dark, is activated by visible light and carbon dioxide is inserted into the aluminium-carbon bond in the presence of *N*-methylimidazole (Im).[4]



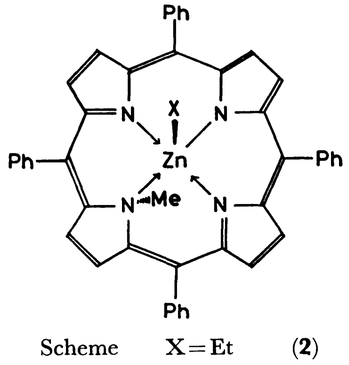
$$\underset{\mathbf{1}}{\mathrm{TPPAlEt}} + \mathrm{CO_2} \xrightarrow[\mathrm{Im}]{h\nu\ (>420\,\mathrm{nm})} \mathrm{TPPAl\text{-}O\overset{}{\underset{\underset{\displaystyle O}{\|}}{C}}\text{-}Et} \qquad (1)$$

The zinc-carbon bond of ethyl(*N*-methyltetraphenylporphinato)zinc (NMTPPZnEt **2**) was found to be subject to homolytic cleavage under irradiation with visible light in dichloromethane solution.[5]

$$\underset{\mathbf{2}}{\mathrm{NMTPPZnEt}} \xrightarrow[\mathrm{in\ CH_2Cl_2}]{h\nu\ (>420\,\mathrm{nm})} [\mathrm{NMTPPZn}\cdot] + \mathrm{Et}\cdot \qquad (2)$$

In these reactions, the metal-carbon bond which may not absorb visible light is indirectly activated by photoexcitation of the porphyrin macrocycle.

In this paper we report the photochemical activation of the zinc-carbon bond of NMTPPZnEt (**2**) in the reaction with thiol having a bulky group, and of the zinc-sulfur bond in porphinatozinc alkyl sulfide (NMTPPZnSR), resulting in the homolytic cleavage of zinc-sulfur bond.



Scheme X=Et (**2**)
SPr^n (**3**)
SBu^t (**4**)
SPh (**5**)
SH (**6**)

Experimental

Materials. Benzene and hexane were distilled under nitrogen over sodium wire. Dichloromethane was refluxed and distilled over calcium hydride under nitrogen. Diethylzinc was distilled under reduced pressure and stored in nitrogen. *N*-Methyltetraphenylporphyrin (NMTPPH) was prepared from α, β, γ, δ-tetraphenylporphyrin and methyl fluorosulfate.[6] NMTPPZnEt (**2**) was prepared by the reaction of NMTPPH and diethylzinc according to the method previously reported.[5] 1-Propanethiol and 2-methyl-2-propanethiol were dried over calcium sulfate (Drierite), distilled and stored under nitrogen. Benzenethiol was dried over calcium sulfate, distilled under reduced pressure, and stored under nitrogen. Hydrogen sulfide was generated by heating "H_2S Powder" (Kanto Chemical Co., Inc.) and used after passing through a column packed with calcium chloride.

Measurements. ^{1}H NMR spectra were recorded using a JEOL-CW-PS-100. Visible spectra were obtained on a JASCO UVIDEC-1 spectrometer. ESR spectra were recorded on a JEOL JES-PE spectrometer under irradiation with visible light (Xe lamp, >420 nm) using nitrosodurene as the radical trapping reagent.

Synthesis of Ethylzinc Propyl Sulfide (EtZnSPr^n). EtZnSPr^n was synthesized according to the method for the preparation of MeZnSPr^n.[7] Diethylzinc (1.10 cm^3, 10.7 mmol) was added to dry, oxygen-free hexane (15 cm^3) in a Pyrex flask (20 cm^3 capacity, fitted with a three-way cock) using a syringe under nitrogen, and the solution was cooled to 0 °C in an ice bath. 1-Propanethiol (0.90 cm^3, 10.0 mmol) was then added dropwise with a syringe to the stirred solution, and the mixture was allowed to warm slowly to room temperature. When gas evolution had ceased, the mixture was heated to reflux to dissolved the solid. The product crystallised on cooling the mixture to room temperature. Ethylzinc propyl sulfide was obtained as colorless short broad needles (1.03 g, 61%), soluble in benzene and dichloromethane. ^{1}H NMR (CH_2Cl_2) δ= 0.36 (2H, q, CH_2-Zn), 0.94 (3H, t, $\underline{CH_3}$-CH_2-Zn), 1.15 (3H, t, $\underline{CH_3}$-CH_2-CH_2-S), 1.66 (2H, m, -$\underline{CH_2}$-CH_2-S), 2.68 (2H, t, -CH_2-S). Found: Zn, 38.3%. Calcd for $C_5H_{12}SZn$: Zn, 38.6%.

Reaction of NMTPPH with EtZnSPr^n. In an attempt to prepare *N*-methyltetraphenylporphinatozinc propyl sulfide (NMTPPZnSPr^n **3**), NMTPPH was allowed to react with an equimolar amount of EtZnSPr^n. NMTPPH (15.7 mg, 0.025 mmol) was dissolved in dichloromethane (1 cm^3) under nitrogen in a Pyrex tube (10 cm^3 capacity) wrapped in aluminium foil and equipped with a three-way cock, and a dichloromethane solution (0.1 cm^3) of EtZnSPr^n (0.025 mmol) was added using a syringe at room temperature in the dark. The reaction mixture was transferred to an NMR tube with a syringe under nitrogen in the dark and subjected to NMR analysis. The NMR investigation indicated that $\mathrm{EtZnSPr}^n$ can react with NMTPPH by both zinc-ethyl bond and zinc-propylthio bond to give $\mathrm{NMTPPZnSPr}^n$ (**3**) and NMTPPZnEt (**2**), respectively (Eqs. 3 and 4), and the propylthio group is substituted for the ethyl group of NMTPPZnEt (**2**) thus formed (Eq. 5).

$$\mathrm{NMTPPH} + \mathrm{EtZnSPr}^n \rightarrow \mathrm{NMTPPZnSPr}^n + \mathrm{EtH} \qquad (3)$$

$$\mathrm{NMTPPH} + \mathrm{EtZnSPr}^n \rightarrow \mathrm{NMTPPZnEt} + \mathrm{Pr}^n\mathrm{SH} \qquad (4)$$

$$\mathrm{NMTPPZnEt} + \mathrm{Pr}^n\mathrm{SH} \rightarrow \mathrm{NMTPPZnSPr}^n + \mathrm{EtH} \qquad (5)$$

The last reaction suggests a good procedure for the formation of NMTPPZnSR, as described below.

Reaction of NMTPPZnEt (2) with Thiol (RSH). To a benzene solution (1 cm^3) of NMTPPZnEt (**2**) (0.025 mmol) was added 1-propanethiol (0.09 cm^3, 1 mmol), 2-methyl-2-propanethiol (0.11 cm^3, 1 mmol), or benzenethiol (0.10 cm^3, 1 mmol) using a syringe in nitrogen at room temperature. The resulting mixture was stirred for an hour in the dark. Removal of the solvent and unreacted thiol under reduced pressure at room temperature left a green solid, which was dissolved in benzene or dichloromethane and subjected to NMR analysis.

Reaction of NMTPPZnEt (2) with H_2S. Hydrogen sulfide was bubbled through a benzene solution (1 cm^3) of NMTPPZnEt (**2**) (0.025 mmol) for 5 min. After being stirred for an hour at room temperature in the dark, the solution was evaporated under reduced pressure to give green powder as the residue; this was dissolved in benzene and subjected to NMR analysis.

Reaction of NMTPPZnEt (2) and $\mathrm{Bu}^t\mathrm{SH}$ under Irradiation. To a benzene solution (0.4 cm^3) of NMTPPZnEt (**2**) (0.01 mmol) in an NMR tube, a benzene solution (0.04 cm^3) of 2-methyl-2-propanethiol (0.01 mmol) was added using a syringe under nitrogen in the dark. The reaction was carried out under irradiation using 500 W Xe lamp (Ushio UXL-500 D-O). The distance between the NMR tube and the lamp was about 30 cm, and a glass filter was used to cut the light of wave length shorter than 420 nm. After the prescribed time of irradiation, the ^{1}H NMR spectrum of the reaction mixture was measured in the dark. The conversion of NMTPPZnEt (**2**) was determined on the basis of the signal intensities due to ethyl protons of **2** and *N*-methyl protons.

Results and Discussion

Photochemical Activation of Zinc-Carbon Bond of NMTPPZnEt (2) in the Reaction with Thiol. The reaction of NMTPPZnEt (**2**) with a large excess of thiol RSH ($\mathrm{R}=\mathrm{Pr}^n$, Bu^t, Ph) in the dark in benzene was examined by inspecting the ^{1}H NMR spectrum of the reaction mixture (Fig. 1). The reaction generally proceeded rapidly at room temperature. The signals due to ethyl protons of NMTPPZnEt (**2**) ($\delta=-2.10$ (t), -5.00 (q)) disappeared, and new signals due to strongly shielded protons ascribed to alkylthio (or arylthio) group appeared at much higher magnetic field than those of thiol (Table 1), indicating that alkylthio (or arylthio) group is attached to the zinc atom in the porphyrin ring and is affected by its ring current. The equimolar ratio of the alkylthio (or arylthio) group and the *N*-methyl group of the porphyrin was confirmed on the basis of the signal intensities of their protons. The visible spectrum of the reaction mixture changed from that of NMTPPZnEt (**2**) (Table 2). These results suggest that NMTPPZnEt (**2**) reacts with thiol to form a porphinatozinc alkyl (aryl) sulfide. Similarly, the reaction of NMTPPZnEt (**2**) with hydrogen sulfide was found to give a porphinatozinc hydrogensulfide.

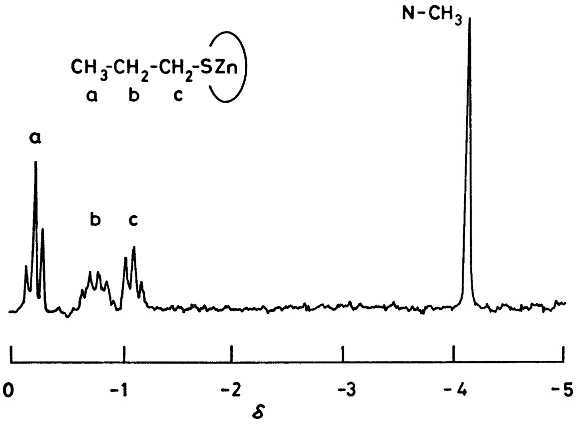


Fig. 1. ^{1}H NMR spectrum of the reaction mixture of NMTPPZnEt (**2**) and $\mathrm{Pr}^n\mathrm{SH}$ in benzene.

$$\mathrm{NMTPPZnEt} + \mathrm{RSH} \rightarrow \mathrm{NMTPPZnSR} + \mathrm{EtH} \qquad (6)$$

$$(\mathrm{R}=\mathrm{Pr}^n,\ \mathrm{Bu}^t,\ \mathrm{Ph},\ \mathrm{H})$$

The reaction of NMTPPZnEt (**2**) was rather slow in the case of a thiol with bulky group such as 2-methyl-2-propanethiol ($\mathrm{Bu}^t\mathrm{SH}$). For example, when NMTPPZnEt (**2**) was allowed to react with $\mathrm{Bu}^t\mathrm{SH}$ in an equimolar ratio at room temperature in the dark, it was found by ^{1}H NMR spectroscopy that the conversion of NMTPPZnEt (**2**) was 21% after 25 min. On the other hand, the substitution reaction was accelerated by irradiation with visible light (Fig. 2); NMTPPZnEt (**2**) reacted with $\mathrm{Bu}^t\mathrm{SH}$ completely under irradiation after 20 min, and $\mathrm{NMTPPZnSBu}^t$ (**4**) was

Table 1. ^{1}H NMR data of NMTPPZnSR[a)]

NMTPPZnSR	Chemical shift δ (Intensity, Multiplicity)	
R	Protons of R	Protons of *N*-CH_3
$CH_3CH_2CH_2$- (**3**)	−0.20(3H, t), −0.74(2H, m), −1.06(2H, t)	−4.12(3H, s)
$(CH_3)_3C$- (**4**)	−0.92(9H, s)	−4.20(3H, s)
C_6H_5- (**5**)[b)]	+6.34(1H, t), +6.10(2H, t), +3.90(2H, d)	−4.07(3H, s)
H- (**6**)	−6.96(1H, s)	−3.97(3H, s)

a) Measured at room temperature in benzene (except for **5**), 2.5×10^{-2} mol dm^{-3}. b) Measured in dichloromethane.

TABLE 2. VISIBLE SPECTROSCOPIC DATA OF NMTPPZnSR[a)]

R	λ_{max}/nm ($\varepsilon \times 10^{-3}$)				
	Soret				
Pr^n (**3**)	438(230) 450(sh)	530(sh)	567(6.8)	619(12)	661(7.2)
Bu^t (**4**)	438(190) 450(sh)	528(sh)	566(6.3)	615(9.2)	661(5.5)
Ph (**5**)	438(180) 450(sh)	530(sh)	566(4.8)	619(8.4)	661(5.1)
H (**6**)	438(230) 450(sh)	527(sh)	565(7.7)	616(12)	661(6.9)

a) Measured in dichloromethane (5×10^{-4}—5×10^{-5} mol dm^{-3}) at room temperature under nitrogen. The optical pathlength was 0.1 cm. b) sh: shoulder inflection.

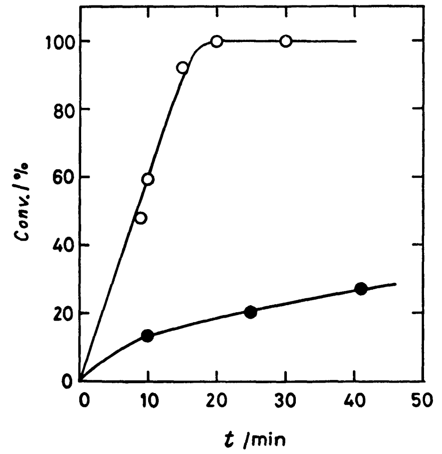


Fig. 2. Formation of NMTPPZnSBu^t by the reaction of NMTPPZnEt (**2**) and Bu^{t}SH at room temperature in benzene. ○: Under irradiation, ●: in the dark. [NMTPPZnEt] = [Bu^{t}SH] = 0.01 mmol. Conversion of NMTPPZnEt was determined by ^{1}H NMR spectrum on the basis of ethyl protons of NMTPPZnEt and N-CH$_3$ protons.

found to be the sole product on the basis of the ^{1}H NMR spectrum of the reaction mixture.

Thus, irradiation with visible light has an interesting effect in enhancing the nucleophilicity of the ethyl group of NMTPPZnEt (**2**) in the reaction with thiols.

Photochemical Cleavage of Zinc-Sulfur Bond in Porphinatozinc Alkyl Sulfide (NMTPPZnSR). N-Methyltetraphenylporphinatozinc propyl sulfide (NMTPPZnSPr^n **3**) was found to be decomposed in dichloromethane by the irradiation with visible light, although it was stable under nitrogen in the dark. The ^{1}H NMR spectrum of NMTPPZnSPr^n (**3**) showed that the intensity of signals due to propylthio group decreased upon irradiation, while the signals due to dipropyl disulfide appeared [^{1}H NMR (CH$_2$Cl$_2$) δ= +0.80 (6H, t), +1.54 (4H, m), +2.45 (4H, t)]. When the signals of the propylthio group of NMTPPZnSPr^n (**3**) disappeared completely (2 h), the formation of dipropyl disulfide was quantitative. The main product derived from porphyrin macrocycle is considered to be N-methyltetraphenylporphinatozinc chloride (NMTPPZnCl) on the basis of the chemical shift of N-methyl protons (δ (CH$_2$Cl$_2$) = −3.90[5)]) observed in the irradiated solution.

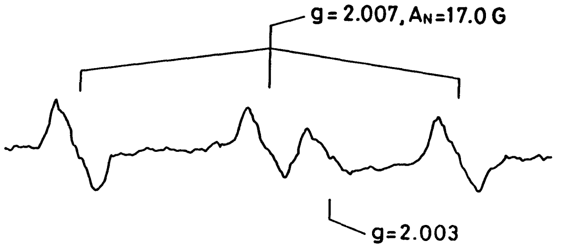


Fig. 3. ESR spectrum of photo-irradiated NMTPPZnSPr^n (**3**) in dichloromethane at r. t. using nitrosodurene as trapping reagent.

$$\underset{\mathbf{3}}{\text{NMTPPZnSPr}^n} \xrightarrow[\text{in CH}_2\text{Cl}_2]{h\nu\ (>420\,\text{nm})} \text{NMTPPZnCl} + \text{Pr}^n\text{SSPr}^n \qquad (7)$$

In contrast with NMTPPZnSPr^n (**3**), EtZnSPr^n was unchanged in dichloromethane under irradiation with visible light. These results indicate that zinc-sulfur bond of NMTPPZnSPr^n (**3**), which does not absorb visible light, is activated by the photoexcitation of the porphyrin ring. In the solution in benzene or in the solid state, NMTPPZnSPr^n (**3**) was found to be almost unaltered by the irradiation with visible light. In the cases of NMTPPZnSBu^t (**4**), NMTPPZnSPh (**5**), and NMTPPZnSH (**6**), the ^{1}H NMR spectra in dichloromethane did not show any change after irradiation with visible light.

Figure 3 shows the ESR spectrum of the dichloromethane solution of NMTPPZnSPr^n (**3**) in the presence of nitrosodurene under visible light. NMTPPZnSPr^n (**3**) did not show any ESR signal in the dark. When the solution of NMTPPZnSPr^n (**3**) in the ESR cavity was irradiated with visible light, two different signals appeared immediately, at g=2.007 (A_N=17.0 G) and g=2.003. The former signal was assigned to propylthio radical trapped by nitrosodurene.[8)] The g value of the latter radical was in agreement with that observed in the irradiation of NMTPPZnEt (**2**) with visible light.[5)]

$$\underset{\mathbf{3}}{\text{NMTPPZnSPr}^n} \xrightarrow[\text{in CH}_2\text{Cl}_2]{h\nu\ (>420\,\text{nm})} [\text{NMTPPZn}\cdot] + \text{Pr}^n\text{S}\cdot \qquad (8)$$

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