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PHOTOCHEMICAL REACTION OF N-METHYL-α,β,γ,δ-TETRAPHENYLPORPHINATOZINC ETHYL. HOMOLYSIS AND SUBSTITUTION WITH VISIBLE LIGHT

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N-Methyl-α,β,γ,δ-tetraphenylporphinatozinc ethyl undergoes the homolytic cleavage of the ethyl-zinc group in methylene chloride by the excitation of the porphyrin ring with visible light, resulting in the substitution of a chlorine for the ethyl group.

Photochemistry of metalloporphyrins is of much interest in connection with the system which converts solar energy into chemical energy. However, few investigations have been undertaken as to the metalloporphyrins having an alkyl group bound to the metal via σ-bond as axial ligand. Photo-activation of the metal-alkyl group is of fundamental as well as practical interest, leading to, for example, photocatalytic reactions. The present communication describes a novel and very interesting effect of visible light on the reactivity of the metal-alkyl bond of N-methyl-α,β,γ,δ-tetraphenylporphinatozinc ethyl (NMTPPZnEt).

NMTPPZnEt was prepared by the reaction between N-methyl-α,β,γ,δ-tetraphenylporphyrin (NMTPPH)[1)] and diethylzinc ($ZnEt_2$). Typically, NMTPPH (31.5 mg, 5.0×10^{-5} mol) was dissolved in methylene chloride or benzene (4.5 ml) in N_2 in a Pyrex tube wrapped with black paper and aluminium foil, then was added by a stoichiometric amount of diethylzinc dissolved in methylene chloride or benzene (0.5 ml) with a syringe. The mixture was stirred for 10-20 minutes at room temperature in the dark. Figure 1a shows ^{1}H-NMR spectrum of the reaction mixture of NMTPPH and $ZnEt_2$ in equimolar ratio. Methylene (-zinc) and methyl signals of ethyl-zinc group were found at δ -6.0 (quartet), and δ -2.9 (triplet), respectively, much higher magnetic field compared with the methylene (δ -0.1) and methyl (δ 1.1) signals of diethylzinc.

This fact clearly indicates that the ethyl group is attached to the central zinc atom as an axial ligand and is affected by the ring current of the porphyrin ring. The signal due to the N-methyl group shifted to δ -4.00 from δ -4.11 in NMTPPH by the reaction with $ZnEt_2$. The intensity ratio of the signals due to the protons of the porphyrin ring, N-methyl group, and ethyl (-zinc) group was found to be 28:3:5. In the equimolar reaction between NMTPPH and $ZnEt_2$ in the dark, the stoichiometric evolution of ethane was observed, as identified by gas chromatography and volumetrically. From these results, N-methyl-α,β,γ,δ-tetraphenylporphinatozinc ethyl is considered to be formed rapidly and quantitatively by the reaction between NMTPPH and $ZnEt_2$ in the dark (1).

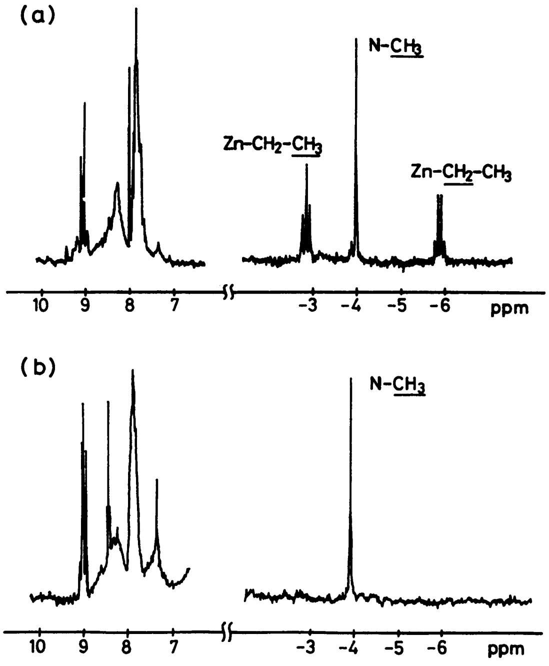
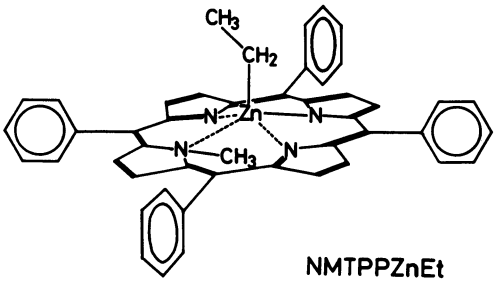


Figure 1. 100 MHz ^1H-NMR spectra in CH_2Cl_2 of the reaction mixture between NMTPPH and $ZnEt_2$ (NMTPPZnEt), NMTPPH 1.0×10^{-2}, $ZnEt_2$ 1.0×10^{-2}; (a) in the dark, (b) after 5 hrs irradiation (>420 nm).

$$\mathrm{NMTPPH} + \mathrm{ZnEt_2} \longrightarrow \mathrm{NMTPPZnEt} + \mathrm{EtH} \qquad (1)$$

Although NMTPPZnEt was stable in N_2 in the dark, it was found to be decomposed by the irradiation with visible light. When the solution of NMTPPZnEt was irradiated with Xe lamp (500 W), cutting the light of wavelength shorter than 420 nm with a filter, the ^1H-NMR signal of the ethyl group bound to the central zinc atom disappeared after 5 hrs (Fig. 1b), accompanied with evolution of ethane. The signal due to the N-methyl group at δ -4.00 also decreased under irradiation, while a new signal appeared and increased at δ -3.90. The extent of the decrease with irradiation time in the signal intensities of the ethyl group and of the N-methyl group (δ -4.00) was in good agreement, keeping the ratio 5:3 throughout the irradiation. When the disappearance of the signals due to the ethyl group was complete, the intensity of the new signal due to N-methyl group (δ -3.90) was 2.4



NMTPPZnEt

with respect to the porphyrin ring protons (28), and no change was observed by further irradiation. In CD_2Cl_2, the decrease in the signals due to the ethyl group was slower than in CH_2Cl_2. This fact suggests that CH_2Cl_2 is the source of hydrogen atom with which the ethyl group from NMTPPZnEt combines and results in the formation of ethane. The main product of the photodecomposition of NMTPPZnEt in CH_2Cl_2 was found to be N-methyl-α,β,γ,δ-tetraphenylporphinatozinc chloride2) (NMTPPZnCl), on the basis of ^{1}H-NMR [δ -3.90 (s N-CH_3) 7.78 (m, phenyl-m, p) 8.20 (m, phenyl-o) 8.34 (s, pyrrole-β) 8.90 (m, pyrrole-β)] and visible spectra (λmax 561,613,660 nm) of the irradiated product. NMTPPZn· transiently generated by the photolysis of the zinc-ethyl group of NMTPPZnEt is considered to abstract a chlorine atom from the solvent CH_2Cl_2 to form NMTPPZnCl.

When the benzene or methylene chloride solution of NMTPPZnEt containing an excess of nitrosodurene (ND) or phenyl-N-tert-butylnitrone (PBN) as a spin trapping agent was irradiated with visible light, the ESR spectrum of the solution in the initial stage of the irradiation at room temperature (Fig. 2a) showed the signal due to the spin adduct radical generated by trapping ethyl radical with ND or PBN (when ND was used, g value=2.006, A_N=13.8 G, $A_{\beta\text{-}H}$=2.8 G; ref.3) g value=2.006, A_N=13.8 G, $A_{\beta\text{-}H}$=3.0 G, and when PBN was used, g value=2.006, A_N=14.6 G, $A_{\beta\text{-}H}$=3.4 G; ref.4), A_N=14.7 G, $A_{\beta\text{-}H}$=3.3 G). Figure 2b shows the ESR spectrum of the solution of NMTPPZnEt after 10 minutes

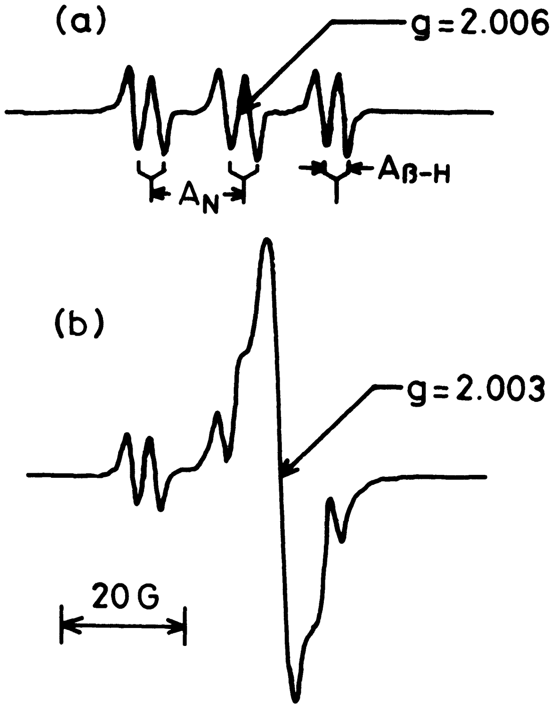


Figure 2. ESR spectra of NMTPPZnEt in the presence of phenyl-N-t-butylnitrone (PBN) in benzene under irradiation (>420 nm). NMTPPZnEt 2.0×10^{-2}M, PBN 2.0×10^{-1}M; (a) the initial stage of irradiation, (b) after 10 minutes irradiation.

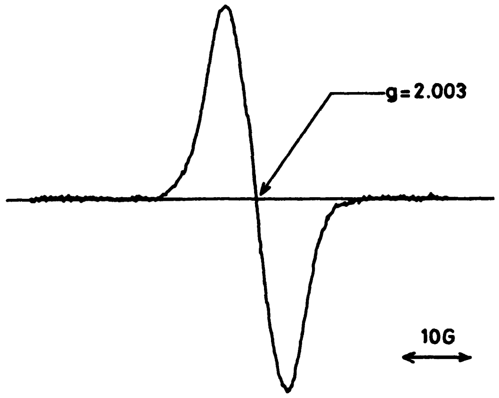
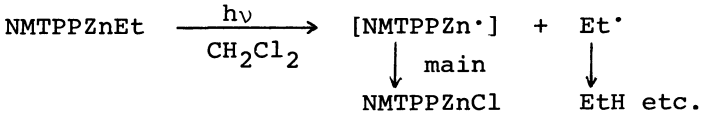


Figure 3. ESR spectrum of NMTPPZnEt in benzene under irradiation (>420 nm); NMTPPZnEt 2.0×10^{-2}M.

irradiation in the presence of PBN. The spectrum consists of two kinds of signals; one of them with a g value of 2.006 is due to ethyl radical as mentioned above, and the intensity of this signal increased in the initial stage of the irradiation then decreased after reaching a maximum. Ethyl radical probably reacts with the spin adduct radical more efficiently than with the spin trapping agent. The other signal is due to an unidentified radical with a g value of 2.003, which is so stable that it could not be trapped by neither PBN nor ND, and the intensity of this signal increased with irradiation then reached a constant. The latter signal was also observed in the ESR spectrum of the solution of NMTPPZnEt with irradiation even in the absence of any spin trapping agent as shown in Figure 3, and is probably assigned to a metalloporphyrin radical, though not established as yet. In the dark, on the other hand, NMTPPZnEt did not show any ESR signal. Neither NMTPPH nor $ZnEt_2$ gave any radical even under irradiation.

From the results mentioned above, the photoreaction of NMTPPZnEt in methylene chloride under irradiation with visible light is considered to proceed as follows (equation (2)):



$$\begin{tikzcd} \mathrm{NMTPPZnEt} \arrow[r, "h\nu", "CH_2Cl_2"'] & {[\mathrm{NMTPPZn}^\bullet]} \arrow[d, "\mathrm{main}"] & + & \mathrm{Et}^\bullet \arrow[d] \\ & \mathrm{NMTPPZnCl} & & \mathrm{EtH\ etc.} \end{tikzcd} \qquad (2)$$

Although the photolysis of alkyl-metal bond is known with some transition metal complexes such as $Co([14]aneN_4)(OH_2)CH_3^{2+}$ 5), the Co-C bond is directly excited even without porphyrin ligand. In sharp contrast, it is of much interest to note that the ethyl-zinc bond of NMTPPZnEt, which may not directly be excited by visible light, is activated by the excitation of the porphyrin moiety, resulting in the homolytic cleavage of the zinc-carbon bond to give NMTPPZnCl in CH_2Cl_2 as the final product, since ethyl-zinc group of diethylzinc or ethylzinc diphenylamide is not photo-decomposed under irradiation with visible light at room temperature.

References

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