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PHOTOCHEMICAL ACTIVATION OF METAL-CARBON BOND IN ZINC AND ALUMINIUM PORPHYRINS. SUBSTITUTION REACTION WITH HINDERED PHENOLS

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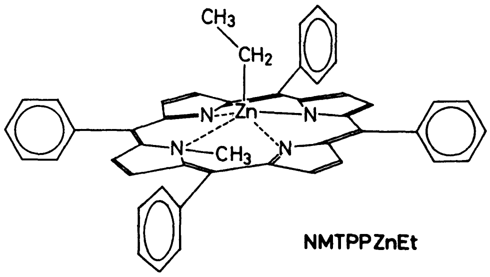
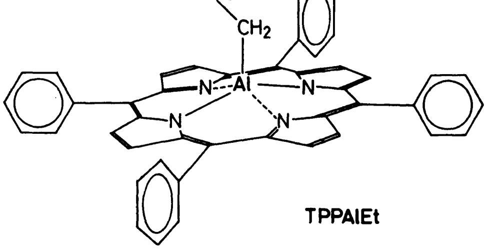
Substitution reactions of N-methyltetraphenylporphinatozinc ethyl and tetraphenylporphinatoaluminium ethyl with hindered phenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-methoxyphenol are accelerated dramatically by the irradiation with visible light, to form the metalloporphyrins with the corresponding phenoxy group bound to zinc and aluminium.

Porphyrin ring is a ligand of particular interest for reactions photo-activated or -sensitized with visible light. Although electron transfer from metalloporphyrin to another substrate has been widely studied, the examples of the activation of the ligand bound to the metal upon irradiation have been very limited. In the course of our studies on photochemical behavior of metalloporphyrins which have an alkyl group bound to the metal via σ bond as axial ligand, the zinc-ethyl bond in N-methyltetraphenylporphinatozinc ethyl (NMTPPZnEt) was found to be homolytically cleaved upon irradiation with visible light in dichloromethane,[1)] while in benzene solution the homolysis proceeded only with difficulty. We now wish to report the novel and dramatic effect of visible light on the reactivity of metal-ethyl bond in NMTPPZnEt and tetraphenylporphinatoaluminium ethyl (TPP-AlEt) in the substitution with hindered phenols


NMTPPZnEt


TPPAlEt

in benzene.

NMTPPZnEt was prepared by the reaction between N-methyl-5,10,15,20-tetraphenylporphine and diethylzinc in benzene under N_2 in the dark.[1)] TPPAlEt was synthesized by reacting 5,10,15,20-tetraphenylporphine with triethylaluminium.[2)] The reaction of NMTPPZnEt or TPPAlEt with hindered phenols such as 2-t-butyl-4-methoxyphenol, o-phenylphenol, o-cyclohexylphenol, 2,6-di-t-butyl-4-methylphenol, and 2,6-di-t-butyl-4-methoxyphenol was carried out in benzene solution under nitrogen atmosphere at room temperature in a Pyrex tube placed in water upon irradiation of visible light with Xe lamp (>420nm; with a filter).

The reaction of NMTPPZnEt with phenols having one ortho substituent was found to proceed readily even in the dark. For example, when a benzene solution of NMTPPZnEt (5.0×10^{-5}mol in 4.5 ml) was added by 1.5 times amount of 2-t-butyl-4-methoxyphenol dissolved in benzene (0.5 ml) and the mixture was stirred for 1 hour under N_2 in the dark, the ^{1}H-NMR spectrum of the resulting mixture as shown in Figure 1 revealed that the signals of the ethyl group bound to the zinc atom in NMTPPZnEt [δ -6.0(q), -2.9(t)] completely disappeared and the intensities of the signals due to the phenol (c,OH; d,aromatic; e,methoxy; g,t-butyl) decreased. The signal due to the N-methyl group of NMTPPZnEt at δ -4.00 disappeared and a new signal assigned to the N-methyl group appeared at δ -4.44 (A). Other four new signals were found at δ 5.5-6.0(m)(D), 3.08(s)(E), 0.8(s)(F), and -0.32(s)(G), where signal F is due to ethane. The intensity ratio of the signals D,E and G is 3:3:9 as compared with the signal intensity of the N-methyl group (A,3H). The intensity

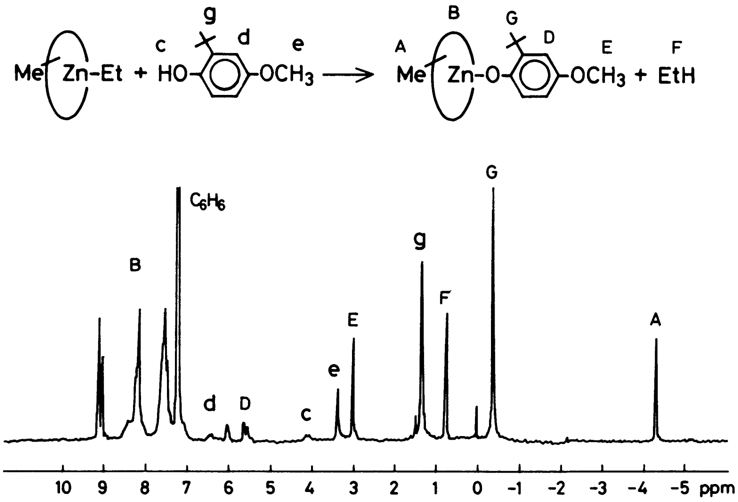
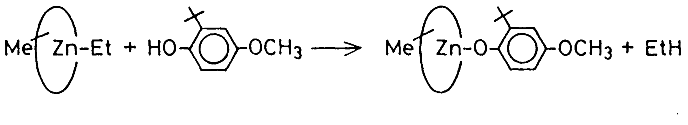


Figure 1. 100MHz ^{1}H-NMR spectrum in C_6D_6 of the reaction mixture between NMTPPZnEt(1.0×10^{-2}M) and 2-t-butyl-4-methoxyphenol(1.5×10^{-2}M) in the dark after 1 hour.

ratio of the sum of the signals d and D, e and E, g and G, respectively, is 3:3:9, indicating that the signals D,E and G are due to the aromatic, methoxy and t-butyl protons, respectively, of phenoxy group bound to the central zinc atom in the reaction product.



The fact that the largest upfield shift affected by the ring current of porphyrin is observed for the t-butyl group (g → G) provides the additional evidence in support of the structure of the reaction product, an N-methyltetraphenylporphinatozinc phenoxide. After completion of the reaction, n-hexane was added to the reaction mixture, the precipitate was separated by filtration, and dried in vacuo at 100°C for 8 hours to give deep green crystals. Found: C,77.07; H,5.58; N,6.40 %. Calcd. for $C_{56}H_{46}N_4O_2Zn$: C,77.12; H,5.28; N,6.43 %. The substitution reaction of NMTPPZnEt with o-phenylphenol or o-cyclohexylphenol also proceeded easily in the dark.

On the other hand, hindered phenols having two bulky groups at both ortho positions such as 2,6-di-t-butyl-4-methylphenol or 2,6-di-t-butyl-4-methoxyphenol hardly reacted with NMTPPZnEt in the dark. However, the reaction proceeded dramatically rapidly upon irradiation with visible light as shown in Figure 2 to form the corresponding metalloporphyrin having zinc-phenoxy group in a virtually quantitative yield, as estimated by the NMR observation of the reaction mixture. In the ESR spectroscopic studies of the reaction mixture between NMTPPZnEt(2.5×10^{-2}M) and 2,6-di-t-butyl-4-methylphenol (1.25×10^{-1}M) upon concurrent irradiation, no phenoxy radical was detected even in the presence of a large excess of phenyl-N-tert-butylnitrone as a spin trapping agent.

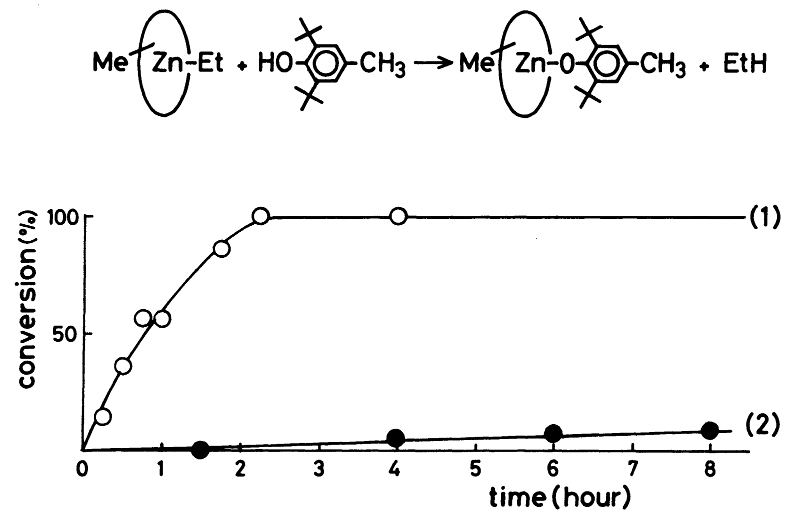


Figure 2. The reaction of NMTPPZnEt(1.0×10^{-2}M) with 2,6-di-t-butyl-4-methylphenol(2.0×10^{-2}M) in C_6D_6 ; conversion as estimated by ^{1}H-NMR signal due to the t-butyl group ; (1) under irradiation, (2) in the dark.

The effect of irradiation with visible light was more remarkable in the reaction of TPPAlEt with phenols. The equimolar reaction between TPPAlEt(5.0×10^{-2} M) and 2-t-butyl-4-methoxyphenol(5.0×10^{-2} M) in benzene proceeded slowly in the dark and was complete after ca.20 hours. The NMR spectrum of the reaction mixture indicated the almost quantitative formation of a metalloporphyrin with a phenoxy group bound to the central aluminium. When 2,6-di-t-butyl-4-methoxyphenol was employed as a hindered phenol, the reaction with TPPAlEt did not occur at all even after a week in the dark. Nevertheless, the reaction proceeded readily upon irradiation with visible light as shown in Figure 3.

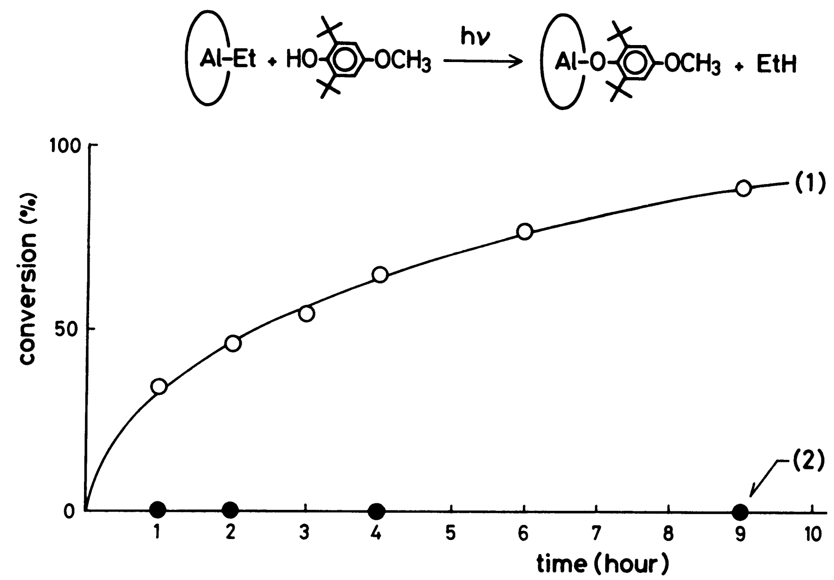


Figure 3. The reaction of TPPAlEt(5.0×10^{-2} M) with 2,6-di-t-butyl-4-methoxyphenol(1.0×10^{-1} M) in C_6D_6 ; conversion as estimated by ^{1}H-NMR signal due to the t-butyl group ; (1) under irradiation, (2) in the dark.

Thus, irradiation with visible light has an interesting remarkable effect on the reactivity of metal-carbon bond in metalloporphyrins of zinc and aluminium in the reaction with hindered phenols. By the excitation of the porphyrin moiety upon irradiation with visible light, the electron density of the ethyl group bound to the central metal is considered to be increased, resulting in the enhanced nucleophilicity of the metal-carbon bond.

References

1) S. Inoue, H. Murayama, N. Takeda, and Y. Ohkatsu, Chem. Lett., 1982, 317.

2) S. Inoue and N. Takeda, Bull. Chem. Soc. Jpn., 50, 984 (1977).

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