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PHOTOCHEMICAL ACTIVATION OF ALUMINUM-ALKYL BOND IN ALUMINUM PORPHYRIN. CONJUGATE ADDITION REACTION WITH VINYL KETONE

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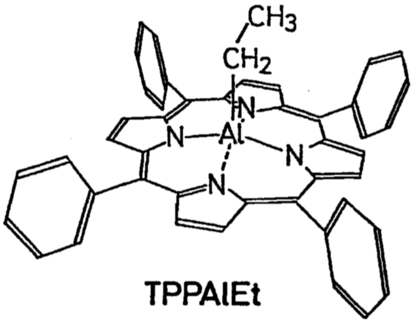
Tetraphenylporphinatoaluminum ethyl undergoes addition reaction toward vinyl ketone via a novel enolate aluminum porphyrin as the intermediate. This reaction is remarkably accelerated upon irradiation with visible light retaining the reaction mode.

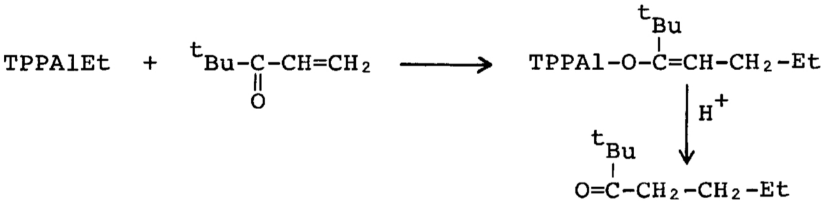
Photochemical activation of metalloporphyrin is a subject of particular interest as an essential elementary process in photocatalytic reactions with visible light, including biological photosynthesis. In the preceding papers, we reported that metalloporphyrins with an axial alkyl ligand is subject to the effect of visible light, in the homolysis of the metal-alkyl bond in dichloromethane[1)] and in the nucleophilic substitution reaction with active hydrogen compounds such as phenol,[2)] or carbamic acid from carbon dioxide and amine.[3)] In this paper we report our novel finding as to the photo-acceleration effect on the addition reaction between tetraphenylporphinatoaluminum ethyl (TPPAlEt)[4)] and vinyl ketones.



TPPAlEt

Expected reactions between TPPAlEt and vinyl ketone are the carbonyl addition to give a carbinol and the conjugate addition to give a saturated ketone via an enolate intermediate. In the ^{1}H-NMR spectrum of the reaction mixture of TPPAlEt and an equimolar amount of tert-butyl vinyl ketone[5)] in $CDCl_3$ after 2 h irradiation with Xe lamp (>420 nm; with a filter) (Fig. 1), signals due to ethyl group of TPPAlEt (δ -6.35 (q, 2H, c), -3.41 (t, 3H, d)) and due to tert-butyl vinyl ketone (δ 6.80 (m, 1H,

b_1), 6.33 (m, 1H, b_2), 5.64 (m, 1H, b_3), 1.21 (s, 9H, a)) decreased. The most remarkable new signal is that at δ -1.46 (e), which is assigned to tert-butyl group present in the vicinity of porphyrin ring and affected by the ring current.[6)] A set of new signals coupled with this is observed (f-i), and the chemical shifts, mode of splitting, and relative intensities indicate that these signals are due to the enolate group bound to aluminum porphyrin resulting from the conjugate addition of TPPAlEt to tert-butyl vinyl ketone; δ -1.46 (s, 9H, e), 1.95 (t, 1H, f), -1.92 (m, 2H, g), -0.04 (m, 2H, h), 0.10 (t, 3H, i).



$$\text{TPPAlEt} + {}^{t}\text{Bu-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH=CH}_2 \longrightarrow \text{TPPAl-O-}\overset{\overset{{}^{t}\text{Bu}}{|}}{\text{C}}\text{=CH-CH}_2\text{-Et} \xrightarrow{H^+} \text{O=}\overset{\overset{{}^{t}\text{Bu}}{|}}{\text{C}}\text{-CH}_2\text{-CH}_2\text{-Et}$$

Another set of small signals j-n indicates the presence of a small amount of 2,2-dimethyl-3-heptanone,[7)] the final product of the conjugate addition, in the reaction mixture. When hydrogen chloride gas was bubbled into the reaction mixture after completion of the reaction, signals assigned to the enolate group disappeared while the signals at δ 2.49 due to 2,2-dimethyl-3-heptanone increased in an

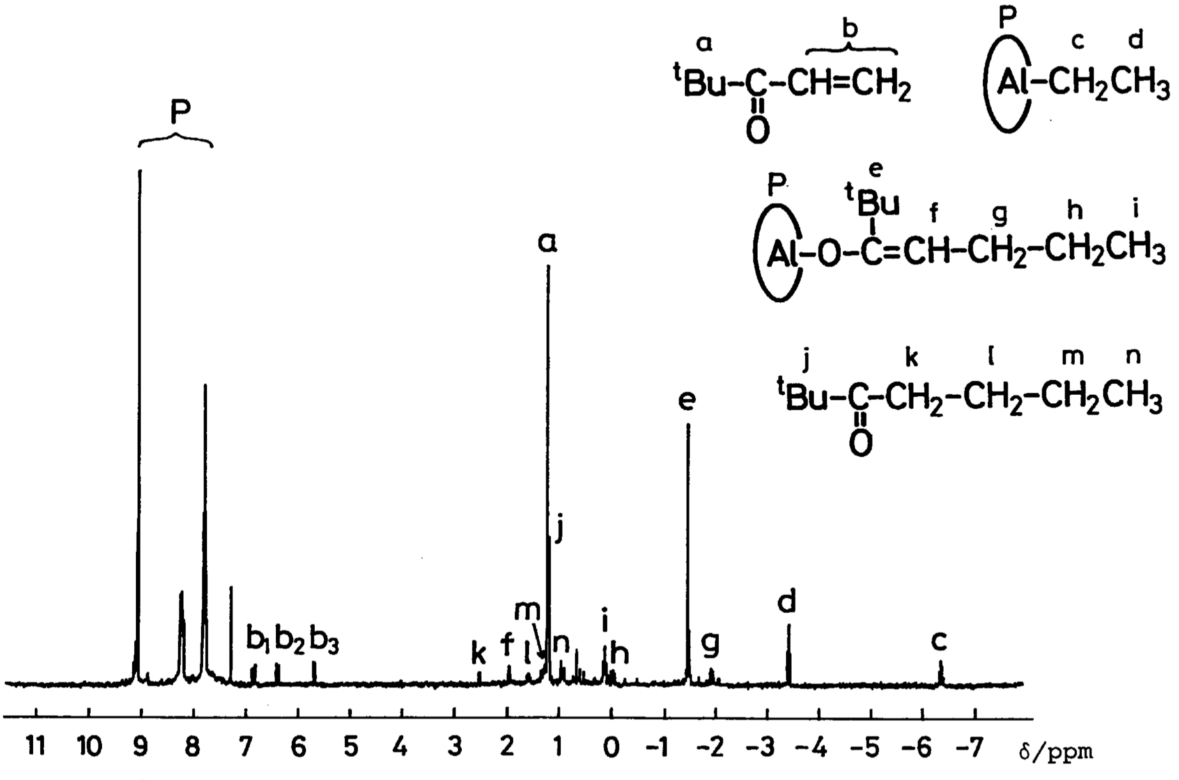


Fig. 1. ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture between TPPAlEt (5.0×10^{-2}M) and tert-butyl vinyl ketone (5.0×10^{-2}M) after 2 h irradiation.

intensity corresponding to about 80% of the enolate group. On the other hand, signals due to 4,4-dimethyl-3-ethyl-1-pentene-3-ol, the product of carbonyl addition, was not detected. Thus, conjugate addition is the exclusive reaction between TPPAlEt and tert-butyl vinyl ketone.

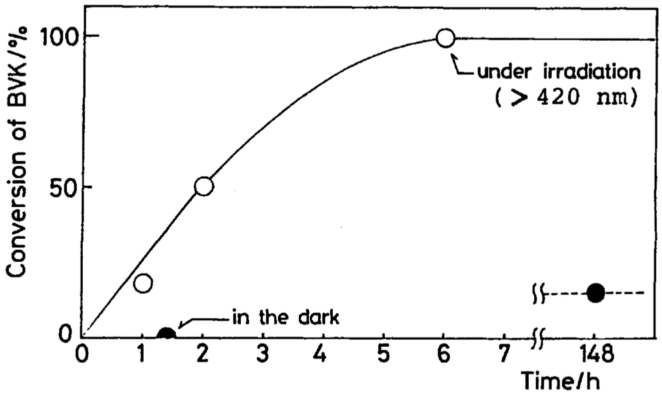


Fig. 2. The reaction between TPPAlEt (5.0 x 10^{-2}M) and tert-butyl vinyl ketone (BVK) (5.0 x 10^{-2}M) in $CDCl_3$; conversion as estimated by ^{1}H-NMR signal due to the vinyl group.

The reaction proceeded only with difficulty in the dark; conversion of tert-butyl vinyl ketone was 15% after 148 h. On the other hand, it completed in 6 h upon irradiation with visible light (Fig. 2).

The reaction between methyl vinyl ketone and TPPAlEt was also slow in the dark, but the addition of N-methylimidazole was found to accelerate the reaction. When a $CDCl_3$ solution of TPPAlEt was added by 3-fold amount of methyl vinyl ketone in the presence of two equivalents of N-methylimidazole (N-MeIm), the ^{1}H-NMR spectrum of the resulting mixture revealed that the signals due to methyl vinyl ketone decreased and those due to ethyl group of TPPAlEt disappeared, while new signals corresponding to 2-hexanone, the final product of conjugate addition, appeared; δ 2.15 (s, 3H), 2.45 (t, 2H), 1.58 (m, 2H), 1.34 (m, 2H), 0.93 (t, 3H). No signal due to ethane was observed, indicating that no hydrogen abstraction by TPPAlEt took place. Even after treatment of the resulting mixture with hydrogen chloride gas, no signal due to 3-methyl-1-pentene-3-ol, the product of carbonyl addition, appeared. Infrared spectrum of the reaction mixture between TPPAlEt and methyl vinyl ketone showed the decrease in the absorption at 1680 cm^{-1} due to the carbonyl group of methyl vinyl ketone with the appearance and increase in the absorption at 1715 cm^{-1} due to the carbonyl group of 2-hexanone. The identity of the resulting product, 2-hexanone, was confirmed by its retention time in GC analysis. The formation of 2-hexanone indicates the participation of an enolate by the conjugate addition between TPPAlEt and methyl vinyl ketone. However, in the system consisting of TPPAlEt, N-MeIm, and methyl vinyl ketone, no signals expected for enolate group bound to aluminum porphyrin was observed in the region of negative δ values in the ^{1}H-NMR spectrum. Aluminum enolate from TPPAlEt and methyl vinyl ketone once formed is considered so reactive to abstract a hydrogen atom from the reactants or the solvent to give 2-hexanone.

Irradiation with visible light brought about an appreciable acceleration of the reaction of TPPAlEt with methyl vinyl ketone. The reaction proceeded to about 20% after 3 h in the dark at room temperature, while it completed after 1 h upon irradiation with visible light, on the basis of ^{1}H-NMR signal intensity of ethyl group in TPPAlEt.8) On the other hand, little change was observed in ^{1}H-NMR and IR spectra of the $CDCl_3$ solution of methyl vinyl ketone (5.0×10^{-1} M) after 4 h irradiation.

Thus alkyl aluminum porphyrin was found to undergo the photo-accelerated, selective conjugate addition toward vinyl ketone to give a novel enolate bound to aluminum porphyrin as the intermediate.

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References

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2) H. Murayama, S. Inoue, and Y. Ohkatsu, Chem. Lett., 1983, 381.
3) S. Inoue, M. Nukui, and F. Kojima, Chem. Lett., 1984, 619.
4) TPPAlEt was prepared from 5,10,15,20-tetraphenylporphyrin and triethylaluminum.2)
5) tert-Butyl vinyl ketone was prepared from pinacolone, paraformaldehyde, and dimethylamine hydrochloride: C. G. Overberger and A. M. Schiller, J. Polym. Sci., 1, 325 (1963).
6) The signal of tert-butyl group in TPPAl-O-CH(t-Bu)-CH_2Cl formed by the reaction between TPPAlCl and 3,3-dimethyl-1,2-epoxybutane is observed at δ -1.48; see also: T. Aida and S. Inoue, J. Am. Chem. Soc., 105, 1304 (1983).
7) δ 1.15 (s, 9H, j), 2.49 (t, 2H, k), 1.55 (m, 2H, l), 1.30 (m, 2H, m), 0.92 (t, 3H, n).
8) The amount of 2-hexanone as detected by ^{1}H-NMR spectrum corresponded to about 60% of the reacted TPPAlEt.

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