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PHOTO-INDUCED CYCLODIMERIZATION OF ELECTRON-RICH AROMATIC OLEFINS IN THE PRESENCE OF TRANSITION METAL COMPLEXES

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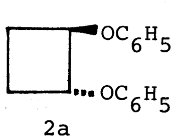
Irradiation of an acetonitrile solution of phenyl vinyl ether in the presence of various metal complexes[Fe(III) and Mn(II) complexes] gave two cyclodimers. Similar irradiation of 1,1-dimethylindene and 1,1-diphenylethylene afforded the corresponding cyclodimers. In these photodimerization, the metal complexes with ligands such as 2,2'-bipyridine and 1,-10-phenanthroline served as catalysts for electron-transfer reaction.

N-Heteroaromatic olefins such as N-vinylcarbazole and its derivatives are known to undergo cyclodimerization via their cation radicals produced by oxidation with metal ions in the dark.1) This reaction can be achieved photochemically by use of Cu(II) ion.2) However, such a reaction of electron-rich aromatic olefins has little been reported.3) We now wish to report the photo-induced cyclodimerization of electron-rich aromatic olefins such as phenyl vinyl ether(**1**), 1,1-dimethylindene(**3**), and 1,1-diphenylethylene (**5**) in the presence of transition metal complexes. In this photoreaction, the metal complexes serve as catalysts for electron-transfer reaction.

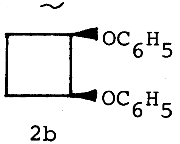
Irradiation of an acetonitrile solution containing **1** and $\mathrm{Fe^{III}(bpy)_3(ClO_4)_3}$ through Pyrex with a 300W high-pressure mercury arc for 40 h under argon gave (2+2) cyclodimers, **2a** and **2b**, approximately in a 1:1 ratio.4) Similarly, irradiation of **3** or **5** in the presence of $\mathrm{Fe^{III}(bpy)_3}$ afforded cyclodimers, **4** and **6**, respectively.3,5) These products were isolated by a column chromatography on silica gel.

Relative yields of the dimers **2a-b** obtained by the use of various metal complexes were determined by GLC analyses. The results are shown in Table 1. The metal complexes with neutral, electron-accepting ligands such as 2,2'-bipyridine(bpy) and 1,10-phenanthroline(phen) are effective, but those with anionic, electron-donating ligands such as acetylacetonato(acac) and tetraphenylporphinato(TPP) were ineffective as catalysts.

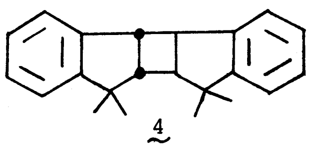
A pale green solution of $\mathrm{Fe^{III}(bpy)_3}$ complex was gradually reduced to a wine red solution of $\mathrm{Fe^{II}(bpy)_3}$ complex in the dark after **1** was added to the former. Fig. 1 shows the change in absorption spectrum of the reaction mixture during this dark reaction: the Fe(III) complex was reduced to the Fe(II) complex, exhibiting an isosbestic point at 600 nm. In the dark, however, cyclodimerization of **1** scarcely occurred. In addition, the photo-induced dimerization of **1** in the presence of $\mathrm{Fe^{III}(bpy)_3}$ was efficiently quenched by the addition of 1,4-dimethoxybenzene which has a lower oxidation potential than that of **1**.



2a



2b



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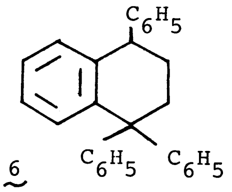

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Table 1. Relative yields in the metal-complex-catalyzed photocyclodimerization of 1[a)]

Metal Complex	ϕ_{rel}	Metal Complex	ϕ_{rel}	Metal Complex	ϕ_{rel}
$Fe^{III}(bpy)_3(ClO_4)_3$	1.0	$Mn^{II}(bpy)_3(ClO_4)_2$	0.65	$Fe^{III}(acac)_3$	0
$Fe^{III}(bpy)_3(ClO_4)_3$	0.07[b)]	$Mn^{II}(phen)_3(ClO_4)_2$	2.37	$FeCl_3$	< 0.01[c)]
$Fe^{II}(bpy)_3(ClO_4)_2$	0.08	$Mn^{III}(acac)_3$	< 0.01	$Fe(NO_3)_3$	< 0.01
$Fe^{III}(phen)_3(ClO_4)_3$	1.30	$Mn^{III}(TPP)Cl$	< 0.01		

a) An acetonitrile solution(5 ml) containing 1(5×10^{-4} mol) and metal complex(5×10^{-6} mol) was irradiated. b) In the dark. c) A Complex mixture was obtained.[3,6)]

These results can be explained in terms of the mechanism shown in Scheme 1. The mechanism involves one electron-transfer from 1 to $Fe^{III}(bpy)_3$, leading to the cation radical of 1($D^{\dagger}$) and $Fe^{II}(bpy)_3$ in the dark(step 1). The cation radical adds to another 1 to produce the dimer cation radical($D_2^{\dagger}$)(step 2). Finally, the electron-transfer from photo-excited $Fe^{II}(bpy)_3$ to $D_2^{\dagger}$ results in the formation of cyclobutanes, 2a-b(step 3). Since the dimerization in the dark is less effective than the photodimerization in the presence of $Fe^{III}(bpy)_3$, the chain process(step 4) proposed by Farid for 1 is unlikely.[4b)]

$$[D] + Fe^{III} \xrightarrow{\text{dark}} [D]^{\dagger} + Fe^{II} \quad (1)$$

$$[D]^{\dagger} + [D] \longrightarrow [D_2]^{\dagger} \quad (2)$$

$$Fe^{II} \xrightarrow{h\nu} {}^{*}Fe^{II} \xrightarrow{[D_2]^{\dagger}} [D_2] + Fe^{III} \quad (3)$$

$$[D_2]^{\dagger} + [D] \longrightarrow [D_2] + [D]^{\dagger} \quad (4)$$

Scheme 1 [D]: Electron-rich aromatic olefin
$[D_2]$: Photocyclodimer

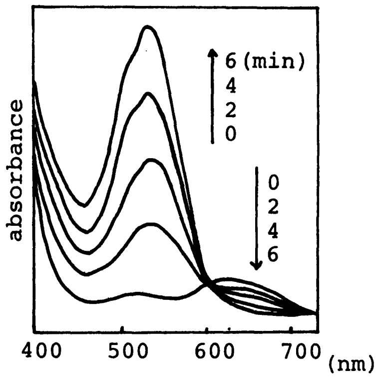

Fig. 1. Spectral change of an acetonitrile solution(4 ml) containing $Fe^{III}(bpy)_3$(5×10^{-4} M) and 1(1×10^{-2} M).

It should be noted here that the dimerization of 1 can little be achieved by oxidation with Fe(III) chloride or nitrate in the dark and even photochemically.[6)] For the photodimerization of electron-rich aromatic olefins, the presence of high-valent metal complexes with electron-withdrawing ligands and photons are essential: the metal complexes serve as a sensitizer for electron-transfer reaction although their detailed function is different from that of organic acceptors such as aromatic nitriles.[4)]

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References and Footnote

1) A. Ledwith, Acc. Chem. Res., 5, 133(1972).

2) M. Asai, H. Matsui, and S. Tazuke, Bull. Chem. Soc. Jpn., 47, 864(1974).

3) S. Farid and S. E. Shealer, J. Chem. Soc., Chem. Commun., 1973, 677.

4) a) S. Kuwata, Y. Shigemitsu, and Y. Odaira, J. Org. Chem., 38, 3803(1973). b) S. Farid, S. E. Hartman, and T. R. Evans, p.327 in "The Exciplex", Academic Press, New York 1975. c) T. R. Evans, R. Wake, and O. Jaeckie, ibid., p.345.

5) R. A. Neunteufel and D. R. Arnold, J. Am. Chem. Soc., 95, 4080(1973).

6) Although an acetonitrile solution of $FeCl_3$ containing 1 was reduced in the dark, the formation of 2a-b scarcely occurred.

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