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PHOTOCHEMICAL REACTIONS OF α-METHYLSTYRENE INDUCED BY Eu(III)/Eu(II) PHOTOREDOX SYSTEM IN METHANOL

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Photoirradiation of a methanol solution of α -methylstyrene and EuCl₃.6H₂O with Pyrex filter resulted in the formation of 2,3-dimethyl-2,3-diphenylbutane and 3,4-dimethyl-3,4-diphenylpentanol in high yields. This reaction was initiated by the excitation of Eu(III)-CH₃OH CT-bands and followed by a successive photochemical reaction of Eu(II) ions formed.

Photochemical reactions of lanthanide ions in homogeneous solutions are attracting much attentions as efficient photoredox systems for harnessing solar energy and also for chemical synthetic processes since they have several stable oxdiation states.¹⁾ Upon illumination of 254 nm light, for example, an aqueous solution of Eu(III) undergoes photoredox reactions in which Eu(II) and OH radicals are formed.²⁾ In the presence of a radical interceptor such as 2-propanol, hydrogen evolution becomes a main process which can be induced by further photochemical reactions of Eu(II).³⁾ However, photochemical studies of lanthanide ions are rather limited to aqueous systems of simple ligand molecules.⁴⁾

Our recent investigations have been focussed on photoredox reactions in homogeneous organic solutions in order to develop a novel type of reaction of synthetic value, such as a fixation of carbon dioxide.⁵⁾ In the course of the investigation we have observed that the photoredox reaction of Eu(III)/Eu(II) in methanol induces an efficient reductive dimerization of styrenes competitively with hydrogen evolution upon illumination of light, λ >300 nm.

Irradiation of a methanol solution of $EuCl_3 \cdot 6H_2O$ (5 mmol·dm⁻³) by use of a high pressure mercury lamp and Pyrex filter resulted in the formation of hydrogen, ethyleneglycol, and formaldehyde. By the addition of α -methylstyrene (1)(50 mmol·dm⁻³) to this system, the formation of hydrogen was reduced and the formation of 2,3-dimethyl-2,3-diphenylbutan (2) and 3,4-dimethyl-3,4-diphenylpentanol (3a) was observed along with a small amount of cumene (5%), and 3-phenylpropanol (2%). After the consumption of 1, hydrogen formation became predominant and the turnover number reached 250 at irradiation of 20 h as shown in Fig. 1.



Fig. 1. Reaction of 1 and hydrogen evolution as a function of irradiation time: $[1]=25 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}]=1 \text{ mmol} \cdot \text{dm}^{-3}$ in 0.1 dm³ methanol (N₂ saturated).

These main products, 2 and 3a, were isolated and characterized by IR, NMR, Mass, and elemental analyses.⁶) The formations of these products were not observed when the photolysis was carried out in acetonitrile nor in the absence of EuCl₃. Another important feature of this reaction is that the wavelength of the effective light is longer than 300 nm (Pyrex filter). Upon irradiation with 254 nm light which is effective for excitation of 1, the reaction did not occur.

In order to get insight of this reaction, the effect of alcohols on the photolysis of the $1-\text{EuCl}_3$ system was examined. In the case of 2-propanol, EuCl_3 was hardly soluble, and after the irradiation a white precipitate separated out. Therefore, 20 vol% of methanol was added in order to increase the solubility for EuCl_3 . The main products were a reductive dimer of 1 (2), and a 2:1 adduct of 1 with the corresponding alcohol (3). The results are shown in Table 1.

Alcohol	Product yie	eld / % b)	Product ratio	H_2/dm^3	CH ₃ CH ₃
	~	3 ~	<u> </u>		$CH_2 CH_2 CH_2 CR^1 R^2 OH$
Methanol	50	24 (3a)	2.1	0.13	3
Ethanol	18	47 (3 b)	0.4	0.50	~
2-Propanol ^{c)}	13	53 $(\tilde{3}c)$	0.2	0.53 ^{d)}	3a: $R^1 = R^2 = H$
a) Irradiati	ion conditio	on: [EuCl ₃ .6	H ₂ O]=5 mmol·dm ⁻	³ , [1]=50	$3D: R^{1}=R^{2}=CH_{3}$

Table 1. Product yields and selectivities in several alcohol^{a)}

a) Irradiation condition: $[EuCl_3 \cdot 6H_2O]=5 \text{ mmol} \cdot dm^{-3}$, $[1]=50 \text{ mmol} \cdot dm^{-3}$, 3 h irradiation. b) Yields are based on the 1 consumed. c) 20 Vol% of methanol was added. d) For the mesurement of the hydrogen formation, methanol was not added.

The results in Table 1 are summarized as follows; i) the yields of 2 decreased in the order of methanol>ethanol>2-propanol, while the yields of adducts (3) and hydrogen formation increased in the order of methanol<ethanol<2propanol, ii) total products yields were not influenced with alcohols (ca. 70%). These observations suggest a competitive reaction of hydrogen atoms, i.e., abstraction of hydrogen from alcohol leading to the formation of a hydrogen molecule and an α -hydroxyalkyl radical, and addition to 1 as shown in Eqs. 2 and 3.

$$H \cdot + R^{1}R^{2}CHOH \longrightarrow H_{2} + R^{1}R^{2}COH (2)$$

$$H \cdot + 1 \longrightarrow Ph \cdot C - CH_{3} (3)$$

$$CH_{3}$$

$$6$$

These primary radicals undergo successive radical addition and radical-radical coupling reactions leading to the formation of the final products.

$$R^{1}R^{2}COH + 1 \longrightarrow Ph-C-CH_{2}CR^{1}R^{2}OH$$
(4)

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The present assumption, that the key intermediate for the final product formation is a hydrogen atom, is consistent with the fact that hydrogen evolution becomes a main and predominant path after 1 has been consumed. This assumption is also supported by the measurement of deuterium isotope effects on the present reactions using deuterated methanols, CD_3OH and CH_3OD . The experimental results can be summarized as follows: i) in the case of CD_3OH , no deuterium atom was incorporated in the product, 2, but two deuterium atoms are present in 3a presumably at the alcoholic α -carbon atom on the basis of fragmentation pattern of the mass spectra, ii) in the case of CH_3OD , on the other hand, two deuterium atoms were incorporated in the product, 2 at C-1 and C-4 positions, and a deuterium atom in 3a at C-5 position, iii) the product ratio, 2/3a, did not vary with CD_3OH but decreased with CH_3OD as shown in Table 2.

Solvent	Product	yield / _% b) 3a ~	Product ratio 2 / 3a
сн _з он	52	20	2.6
сd ₃ он	42	17	2.5
сн _з ор	43	33	1.3

Table 2. Deuterium isotope effects a)

a) Irradiation conditions; $[EuCl_3 \cdot 6H_2O] = 5 \text{ mmol} \cdot dm^{-3}$, $[1]=100 \text{ mmol} dm^{-3}$, 5 h irradiation. b) Yields are based on the 1 consumed.

Important facts derived from these observations are; 1) hydrogen atoms presumed in Eqs. 2 and 3 originate from alcoholic hydrogen (MeO<u>H</u>), probably by the photochemical reduction by Eu(II) ion, 2) in the case of CD_3OH , lack of deuterium isotope effect on the product ratio indicates that hydrogen abstraction from methanol (Eq. 2) does not compete with addition to 1 (Eq. 3). Therefore, the hydroxymethyl radical which results in the formation of 3a might be produced by another path, probably by the initial photochemical oxidation of methanol by

Eu(III) ion as mentioned below. Hydrogen abstraction from alcohol becomes, of course, an important path in ethanol and in 2-propanol on the basis of high yields of **3** and hydrogen molecules, 3) low product ratio, 2/3a observed in CH₃OD might be caused by an increased rate constant of deuterium atom with methanol (Eq. 2) simply because of higher bond energy of HD than that of H₂. It is, however, difficult to conclude at present.

On the basis of these experimental observations, the following rection scheme is presented.



The formation of Eu(II) ions as the key active species for the reduction of 1 was verified by the spectroscopic measurements. An absorption spectrum of methanol solution of EuCl₃ shows band maxima at 230 and 275 nm which are assigned to Eu(III)-MeOH CT-band. After the irradiation of this solution in the presence of 1, new absorption band at 320 nm, which is due to Eu(II) ion, was detected. Emission spectrum of Eu(II) was also observed at 446 nm by addition of 18-crown-6 ether after the irradiation.⁷⁾

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- 6) 2: colorless needles(from MeOH-H₂O), mp 116 °C(lit mp 119 °C [M. S. Kharasch and W. H. Urry, J. Org. Chem., <u>13</u>, 101 (1948)]); ¹H NMR(CDCl₃) δ =1.26(s, 12H), and 6.93(bs, 10H); mass spectrum, m/e 238(M⁺), 119, 103, and 91. 3a: viscous oil, ¹H NMR(CDCl₃) δ =1.29-1.30(s, 9H), 1.66(s, 1H), 1.84-1.93(m, 1H), 2.38-2.46(m, 1H), 3.23-3.49 (m, 2H), and 7.01-7.25(m, 10H); mass spectrum, m/e 268(M⁺), 149, 132, 119, 105, and 91; IR (neat) 3600, 3350, 1370, and 1030 cm⁻¹, Found: C, 81.24, H, 8.47%. Calcd for C₂₁H₂₆O₂(acetylated derivative of 3a): C, 81.25, H, 8.44%. Satisfactory spectral data were obtained for all new compounds. The details will appear in another article.
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