Influences of Lewis Acids on the Photochemical Cyclodimerization of Cyclopentenone

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Synopsis. In the presence of tin(IV) chloride, photochemical dimerization of cyclopentenone gave a cis-transoid-cis head-to-head dimer as predominant product. Other Lewis acids such as zinc(II) bromide, boron trifluoride etherate, tin(II) chloride, and silver(I) trifluoromethylsulfonate, however, showed little influence. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanum(III) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III) affected regiochemistry of the reaction in a way to favor a head-to-tail dimer.

Photochemical (2+2) cycloaddition of cyclopentenones to form tricyclic ring systems has been widely used for the synthesis of natural products.[1] Since these tricyclic compounds are of difficult access via ordinary ionic reactions, photochemical route appears to be more attractive for their preparation. However, photochemical (2+2) cycloaddition is generally known to be difficult to control its regio- and/or stereochemistry and many possible isomers are formed together. In order to improve the selectivity, micellar effect[2] and salt effect[3] have been studied, but no satisfactory results have been obtained as yet. We thought that the coordinative ability of Lewis acids or lanthanoid complexes to carbonyl oxygen may be exploited to control the mode of photochemical cyclodimerization of cyclopentenon in solution.

Results and Discussion

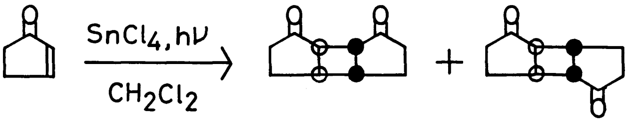
Dry dichloromethane solutions containing 0.6 mol dm^{-3} cyclopentenone (**1**) and various amounts of tin(IV) chloride(**2**) were irradiated using a merry-go-round apparatus with a high-pressure mercury lamp under a nitrogen atmosphere. Product analyses were performed by gas chromatographic comparison with authentic samples[4] and typical results are tabulated in Table 1.

Table 1. Effect of $SnCl_4$ on the Photochemical Dimerization of Cyclopentenone

$SnCl_4$ mole ratio[a]	Time h	Conversion %	Yields/%[b] HH	Yields/%[b] HT	Ratio HH/HT
0.00	5.5	55	15	41	27/73
0.00	2.5	27	19	43	30/70
0.00	0.1	1	20	45	30/70
0.13	5.5	35	13	18	43/58
0.25	5.5	38	14	16	47/53
0.53	5.5	16	24	3	89/11
0.63	5.5	20	9	1	90/10

a) Mole ratio of $SnCl_4$/cyclopentenone. b) Yields are based on cyclopentenone consumed.

As a tendency, the yields of a cis-transoid-cis head-to-tail dimer (HT) decreased while those of a cis-transoid-cis head-to-head dimer (HH) increased as the



1 HH HT

Scheme

Table 2. Relative Rate of Degradation of HH and HT Dimers in the Presence of **2**[a]

2 mole ratio[b]	Time h	Filter	HH %	HT[c] %	HH/HT ratio
0.0	0.0	None	33	67	33/67
0.0	5.0	None	0	34	0/100
0.5	5.0	None	7	38	16/84
0.0	5.5	$CuSO_4$[d]	10	56	15/85
0.5	5.5	$CuSO_4$[d]	20	59	25/75

a) About 0.1 mol dm^{-3} of HH and HT dimer solution in dichloromethane was irradiated and amounts of the dimers were determined by gas chromatography using xanthone as the internal standard. b) Mole ratio of $SnCl_4$/dimers. c) Amounts of HH and HT dimers remained. d) $CuSO_4$; 1 cm thickness of saturated $CuSO_4$ aqueous solution filter.

Table 3. Effect of Lewis Acids on the Photochemical Dimerization of Cyclopentenone

Lewis acid mole ratio[a]	Conversion %	Ratio HH/HT
$ZnBr_2$(0.13)	30	34/66
$ZnBr_2$(0.25)	30	35/65
$ZnBr_2$(0.50)	10	31/69
$BF_3 \cdot OEt_2$(0.30)	40	23/77
$BF_3 \cdot OEt_2$(0.55)	50	38/62
$SnCl_2$(0.50)	30	31/69
AgOTf(0.25)	34	37/63
AgOTf(0.50)	13	53/46
La(thd)$_3$(0.05)	25	20/80
Eu(thd)$_3$(0.05)	23	20/80

a) Mole ratio of the Lewis acid/cyclopentenone.
Tf= trifluoromethanesulfonate
thd = 2,2,6,6-tetramethyl-3,5-heptanedionato

mole ratio (**2**/**1**) changed from zero to 0.53, the HH/HT ratios finally rising up to ca. 9.

Effect of **2** on the photodegradation of the dimers was also studied. No matter whether **2** was present or not, HH dimer was degraded faster than HT dimer (Table 2). Thus, the observed improvement of the selectivity cannot simply be attributed to the preferential degradation of HT dimer by **2**.

Total yields (HH+HT) were not so high and decreased as the conversion increased. It was because that the dimers underwent further photochemical reactions by absorbing light competitively with cyclopentenone.

With an expectation to increase yields by suppression of decomposition of the dimers, cyclopentenone solution was irradiated through $CuSO_4$ filter. HH dimer had the absorption maximum at 300 nm ($\varepsilon \doteqdot 60$) and $CuSO_4$ filter cut off lights shorter than 310 nm. As shown in Table 2, $CuSO_4$ filter suppressed the decomposition, although small amounts of dimers decomposed because of a small overlap of absorption edge of the dimers around 310—320 nm and light through $CuSO_4$ filter. However, the yields of dimers did not increase by using $CuSO_4$ filter, because absorption of cyclopentenone shifted to the shorter wavelength by coordination with **2** (Fig. 1) and cyclopentenone coordinate with **2** was not absorb light through $CuSO_4$ filter efficiently.

Effects of other Lewis acids such as zinc(II) bromide, boron trifluoride etherate, tin(II) chloride, and silver(I) trifluoromethanesulfonate were also examined in THF solutions. However, no significant influence of these Lewis acids was observed (Table 3). Acidity of these Lewis acids may be too weak to form such a rigid complex with **1** as to effect the regiochemistry.

When a low concentration of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanum(III) (La(thd)$_3$; **3**) or tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III) (Eu(thd)$_3$; **4**) was added to the solution of **1** (mole ratio **3**/**1** or **4**/**1**=0.05), the ratio of regioisomers (HH/HT) decreased a little (Table 3). Addition of the increasing amount of **3** or **4** to the solution resulted in the formation of a complex of **1** with **3** or **4** which did not liberate **1** or its dimers at all under the conditions employed.

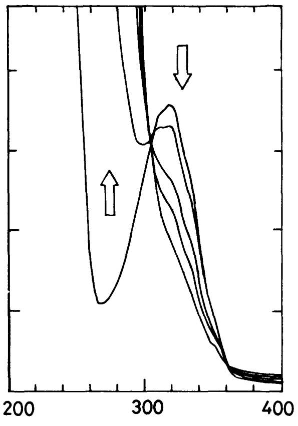


Fig. 1. UV absorption spectra of cyclopentenone in the presence of tin(IV) chloride.[a)]
a) Arrows indicate the direction of spectral changes observed when 0.0 to ca. 0.5 mol ratio of $SnCl_4$ was added to a CH_2Cl_2 solution of cyclopentenone.

The results mentioned above are quite different from those observed in the cases of aromatic enones (cinnamate[5a)] and coumarin[5b)]). In the case of coumarin the quantum yield was highest when 0.125 equiv of boron trifluoride was present, and the predominant dimer was head-to-head in the absence of the Lewis acid, and head-to-tail in the presence of boron trifluoride. It is believed that the excited complex of coumarin with boron trifluoride reacts with another molecule of coumarin at the ground state, leading to the observed dependence of quantum yields on concentration.[5)]

Contrarily, in the case of cyclopentenone small amounts of **2** (**2**/**1**=0.1—0.2) were not effective, and the addition of about 0.5 mol of **2** to 1 mol of **1** was necessary to achieve high HH/HT ratio (Table 1). Furthermore, the regiochemistry changed from head-to-tail to head-to-head by the addition of **2**. These results can be explained by an assumption that two molecules of cyclopentenone coordinate on one tin(IV) chloride from one side through the carbonyl oxygen atom and the photochemical dimerization occurs within the complex thus formed. Formation of 1:2 complex of **2** with **1** was supported by UV absorptivity change of **1** in the presence of various mole ratio of **2** (Fig. 2). The 1:2 complex formation is in consistent with the favored head-to-head regiochemistry in the presence of **2**, because the most favored conformation of two molecules of **1** in the complex would give the head-to-head dimer.

If the photochemical reaction occurs between the Lewis acid complex of **1** and non-coordinated **1**, the effect should be observed even at low Lewis acid/cyclopentenone ratio as was the case with coumarin. Coordinated cyclopentenone would be unable to react with ground state cyclopentenone by two reasons; small absorptivity of coordinated cyclopentenone as is shown in Fig. 1 and steric crowding around the tin(IV) atom.

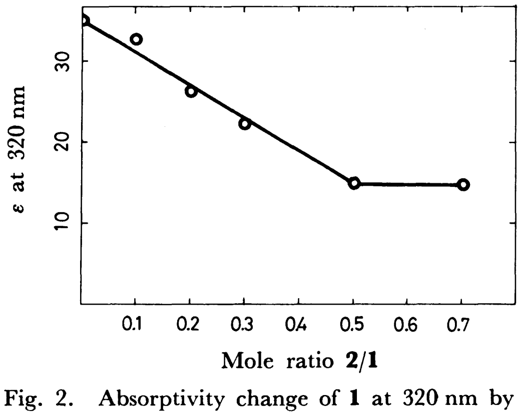


Fig. 2. Absorptivity change of **1** at 320 nm by adding various mole ratio of **2**.

Experimental

Materials. Cyclopentenone was prepared according to the reported method.⁶⁾ Tin(II) chloride, zinc(II) bromide, boron trifluoride etherate and silver(I) trifluoromethanesulfonate were commercial products and used as such. Lanthanoid complexes were prepared according to the literature method.⁷⁾ Dichloromethane was dried over P_2O_5, distilled under nitrogen, and stored with molecular sieves 3A.

Irradiation of Solutions. About 6 mmol of **1** and the Lewis acid were dissolved in 10 dm^{-3} of dry dichloromethane and were irradiatd under a nitrogen atmosphere in Pyrex tubes, using a 300-W high-pressure mercury arc lamp. In instances where equal irradiation of several samples was required, a merry-go-round apparatus was used.

Products Analyses. Dimer ratios and relative yields were analyzed by gas chromatography, using a 20% PEG-6000 (1 m) or 25% DEGS (1 m) column, and xanthone was used as an internal standard. Column temperature was 170 °C. Retention times of samples were as follows. In the case of PEG-6000: **1**, 11 min; HT, 27 min; HH, 38 min. In the case of DEGS: **1**, 3 min; HT, 6 min; HH, 9 min.

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