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Pericyclic Reactions of Cyclopentadienones with Nonactivated Olefins in Phenolic Solvents. Enhancement of the Reactivity and Periselectivity

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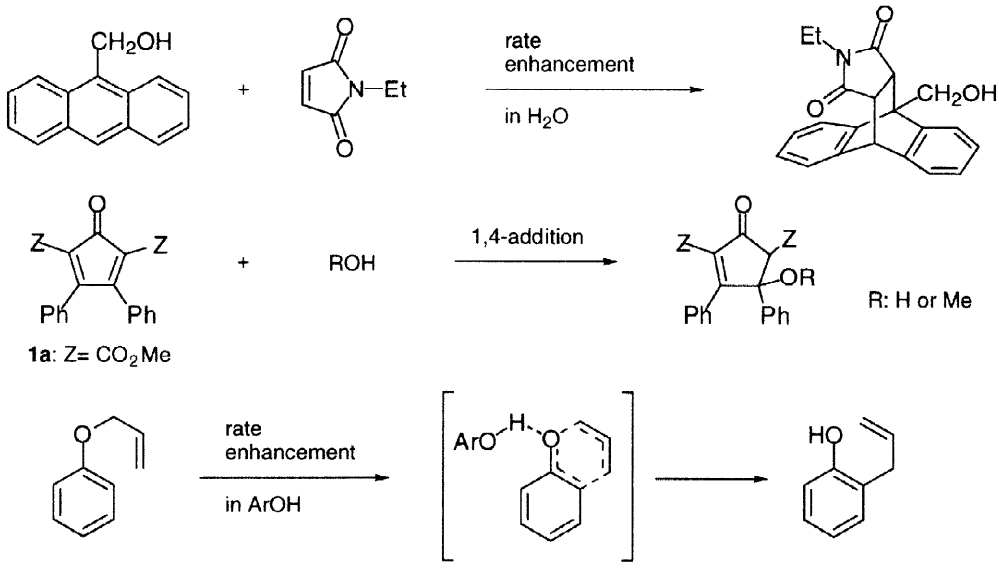
Abstract: The solvent effect of phenols on the reactivity and periselectivity for the pericyclic reactions of cyclopentadienones with olefins involving conjugated medium-ring polyenes has been investigated. The use of phenols as a solvent accelerates the reaction rates of cycloadditions of cyclopentadienones with nonactivated olefins. In the reaction of cycloheptatriene in *p*-chlorophenol, the *exo* [4+6]π cycloadduct was produced predominantly, in which a 15-fold increase of the reaction rate was observed as compared with that in benzene. The [3,3]-sigmatropy and decarbonylation of the primary cycloadducts were also accelerated by phenols. The possible role of phenols is discussed on the basis of kinetic and molecular orbital (MO) calculation data. © 1999 Elsevier Science Ltd. All rights reserved.

Pericyclic reactions normally show only small solvent rate effects because the reactions proceed through a mechanism which involves very little change in charge separation between the ground state and the transition state.[1a] Therefore, pericyclic reactions in polar solvents have been considered to be unfavorable because of higher activation energies than those in nonpolar solvents due to additional desolvation energies of the reactants. Recently, remarkable accelerations of some Diels-Alder (DA) reactions in aqueous solutions have been reported, in which the hydrophobic effect is of principal importance.[1b] However, "the hydrophobic effect" cannot be expected for dienes like cyclopentadienones because active cyclopentadienones such as 2,5-*bis*



Scheme 1

PII: S0040-4020(99)00259-8

(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) react with hydroxylic solvents to give the corresponding 1,4-adducts.[2]

During the course of the studies of pericyclic reactions of olefinic xanthates, we found that the presence of a large excess of a phenol [3] altered the reaction mechanism or significantly accelerated the reaction rate (Scheme 1). Based on these findings together with the fact that the *ortho*-Claisen rearrangement of allyl *p*-tolyl ether is accelerated by phenols,[4] we have undertaken a study of the pericyclic reactions of cyclopentadienones with unsaturated compounds in phenolic solvents. [5]

This paper describes the overall aspects of the solvent effects of *p*-chlorophenol (PCP) on the cycloadditions of some 2,5-disubstituted-3,4-diphenylcyclopentadienones with various olefins involving conjugated medium-ring polyenes and the subsequent pericyclic reactions of the cycloadducts.[6]

Results

Cycloadditions with General Olefins The solvent effect of PCP on the cycloadditions of **1a** with various olefins which have no electron-attracting functional groups in conjugation with a C=C bond was studied. The results are summarized in Table 1. Significant shortening of the reaction time was observed in each case. With dienophiles like 1,5-cyclooctadiene (**2e**) and styrene (**2a**), [7,8] a moderate rate enhancement was observed on changing the solvent from benzene to PCP. Cyclohexene (**2d**) which is known to be a very inactive dienophile reacted with **1a** in PCP at 80 °C to give the DA adduct, while no DA adduct was obtained in benzene. The use of the dienophile as solvent gave the DA adduct under the same reaction conditions. [5]

Table 1. Cycloaddition of **1a** with Various Nonactivated Olefins in Benzene and PCP.

olefin	solvent	temp. (°C)	time (h)	yield (%)	ref.
styrene (**2a**)	benzene	r.t.	6	96(*endo*: *exo*=11: 1)	8
	PCP	r.t.	1	91(*endo*: *exo*=4: 1)	
2,4-hexadiene (**2b**)	benzene	60	12	83	5
	PCP	60	3	79	
bicyclo[2.2.1]hepta-2,5-diene (**2c**)	benzene	40	1	96	8
	PCP	40	0.5	94	
cyclohexene (**2d**)	benzene	80	48	0	
	none	80	48	61(*endo*: *exo*=2: 1)	5
	PCP	80	72	88(*endo*: *exo*=1: 1)	
1,5-cyclooctadiene (**2e**)	benzene	80	8	86	7
	PCP	80	3	95	
cycloheptatriene (**2f**)	benzene	60	48	99	11
	PCP	r.t	96	96	
bicyclo[2.2.1]hept-2-ene (**2g**)	benzene	40	2	89	8
	PCP	40	1	87	

In PCP, the yield of the *exo* cycloadducts increased comparison with those for benzene (see the reactions with **2a** and **2d**).

Rate Study The pseudo-first-order rate constants of the reactions in PCP at 40°C were obtained by following the disappearance of the visible absorption of **1a** using UV/Vis spectroscopy. The rate constants and relative rates ($k_{PCP}/k_{benzene}$) for the unsaturated compounds are summarized in Table 2. The rate enhancements

more than 10-fold were observed in the reactions with **2b** and **2f**. In dienophiles like 1-octene (**2h**), cyclooctene (**2i**) and **2a**, an average of 5-fold rate enhancement was observed on changing the solvent from benzene to PCP.

Table 2. Pseudo-first-order Rate Constants (k) for Cycloadditions of **1a** with Dienophiles in Benzene and PCP at 40 °C.

dienophile	k [a] x 10^5 (sec^{-1})		$k_{PCP}/k_{benzene}$	HOMO level [b] (eV)
	in benzene	in PCP		
2a	323.3	1453	4.5	-9.129
2b	7.28	97.4	13.4	-8.916
2c	193.5	1695	8.8	-9.655
2d	0.046[c]	0.37	8.0	-9.593
2e	0.372[d]	2.07	5.6	-9.650
2f	3.26	47.5	14.6	-8.952
2g	37.66	275.4	7.3	-9.655
2h	3.14	19.56	6.2	-10.150
2i	2.32	12.59	5.4	-9.785

a) One hundred equivalents of dienophiles were used at 40°C. b) Calculated by PM3.
c) Estimated from the rate constant at 80°C. d) The 1:2 adduct was produced in 8% yield.

To know the effect of PCP on the cycloadditions, the activation parameters for the cycloaddition of **1a** with **2c** were measured in benzene and PCP solvents (Table 3). The activation entropies for benzene and PCP are -35 and -36 e.u., respectively. The lowering of the activation energy on changing the solvent from benzene to PCP is 1.4 kcal/mol, in harmony with the increase of the observed cycloaddition reactivity.

Table 3. Activation Parameters for the Reaction of **1a** with **2c** in Benzene and PCP.[a]

solvent	Ea (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
benzene	11.8	-35
PCP	10.4	-36

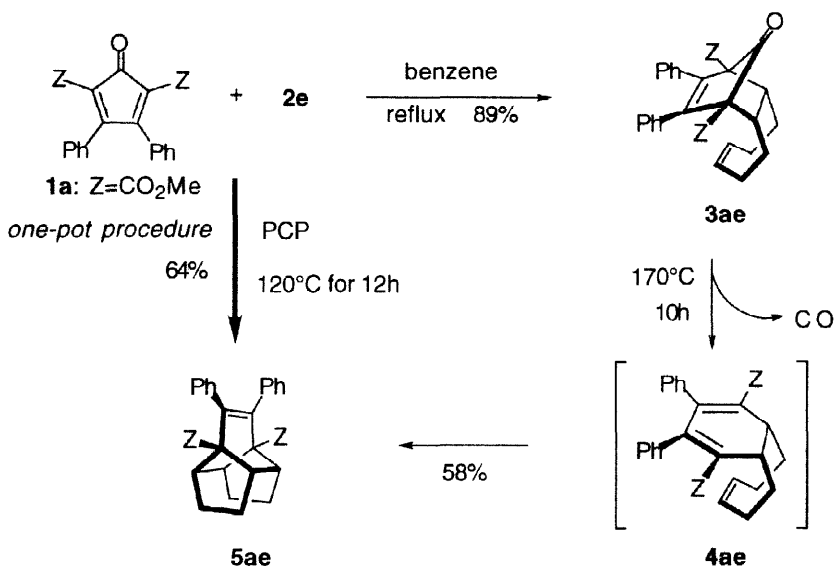
a) The relevant rate constants are collected in Table 9.

The rates of cycloaddition of **1a** with **2c** were found to be affected by the hydrogen-bonding power of solvents, which can be judged from the rate response to the change of Y-values for phenol-benzene solvent system [9] and the substituent effect of phenols (p-cresol < phenol < PCP) (see Table 4).

Table 4. Pseudo-first-order Rate Constants (k) for Cycloadditions of **1a** with **2c** in Phenol-Benzene Solvents at 40°C.

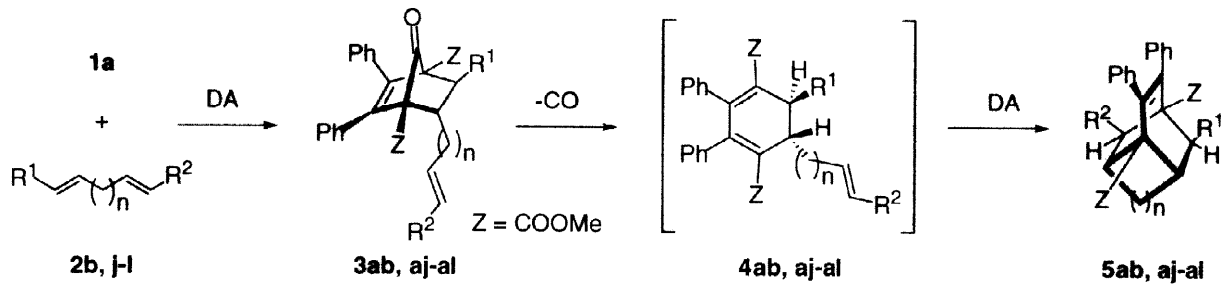
ArOH (W/W%)		$k \times 10^3$ (sec^{-1})	Y value
20%	Phenol	4.33	-0.711
30%	Phenol	4.77	-0.192
50%	Phenol	5.22	0.425
70%	Phenol	5.77	1.101
90%	*p*-Cresol	5.23	
90%	Phenol	6.05	1.427
90%	PCP	6.50	

Double Diels-Alder Reaction The cycloaddition of **1a** with **2e** gave the DA adduct.[7] Thermolysis of the DA adduct at 170°C for 10h gave the double Diels-Alder (DDA) adduct (**5ae**) *via* the decarbonylated DA adduct (**4ae**). Heating a solution of **1a** and **2e** in PCP at 120°C for 12h gave the **5ae** in a one-pot procedure *via* three-step sequential pericyclic reactions which involves intermolecular DA reaction, decarbonylation and intramolecular DA reaction (Scheme 2). This reaction occurred at a temperature *ca.* 50°C lower than that performed without solvent. A rough estimation of the decarbonylation rate based on the half-lives of **3ae** in PCP and *o*-dichlorobenzene indicates that the decarbonylation is over 30-fold faster in PCP than in *o*-dichlorobenzene.



Scheme 2

The cycloadditions of **1a** with both conjugated and nonconjugated linear dienes (**2b, j-l**) gave the *endo* DA adducts (**3ab, aj-al**). [10] The reaction conditions for the formation reaction of DDA adducts (**5ab, aj-al**) are summarized in Scheme 3 and Table 5. As shown in Table 5, the reaction occurred at a temperature *ca.* 40-60°C lower than that performed without solvent. The rate enhancement of the decarbonylation reaction was also observed in PCP solvent.



2b : n = 0, R^1 , R^2 =Me
2j : n = 0, R^1 = Me, R^2 = CO_2Et
2k : n = 1, R^1 , R^2 = H
2l : n = 2, R^1 , R^2 = H

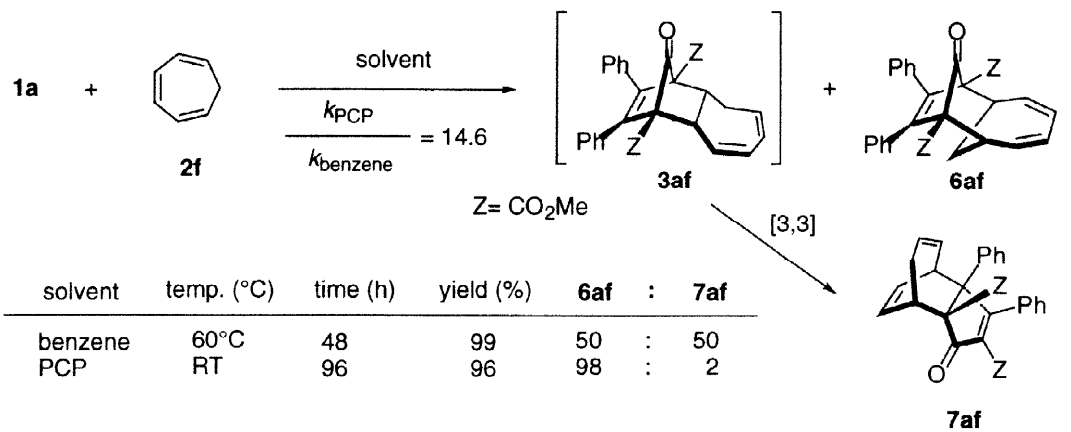
Scheme 3

Table 5. Reaction Conditions for Formation of DDA Adducts (**5ab, aj-al**) from DA Adducts (**3ab, aj-al**).

DA adduct	solvent	temp. (°C)	time (h)	yield (%)	ref.
3ab	none	210[a)]	48	77 (**5ab**)	10
	PCP	150	48	75	
3aj	none	170[a)]	8	64 (**5aj**)	10
	PCP	120	9	53	
3ak	none	200	24	63 (**5ak**)	
	PCP	150	20	75	
3al	none	150	8	70 (**5al**)	7
	PCP	110	9	63	

a) Lowering of the reaction temperature afforded the [3,3]-sigmatropic rearrangement product (see Scheme 6).

Pericyclic Reactions of Conjugated Medium-ring Polyenes To clarify the effect of PCP on the reactivity and periselectivity of conjugated medium-ring polyenes, we examined the cycloaddition of **1a** with **2f**. The reaction of **1a** with **2f** in benzene at 60°C afforded a 1:1 mixture of the *exo* [4+6]π cycloadduct (**6af**) and *endo* [2+4]π cycloadduct (**7af**) derived from the [3,3]-sigmatropic rearrangement of the primary *endo* [4+2]π cycloadduct



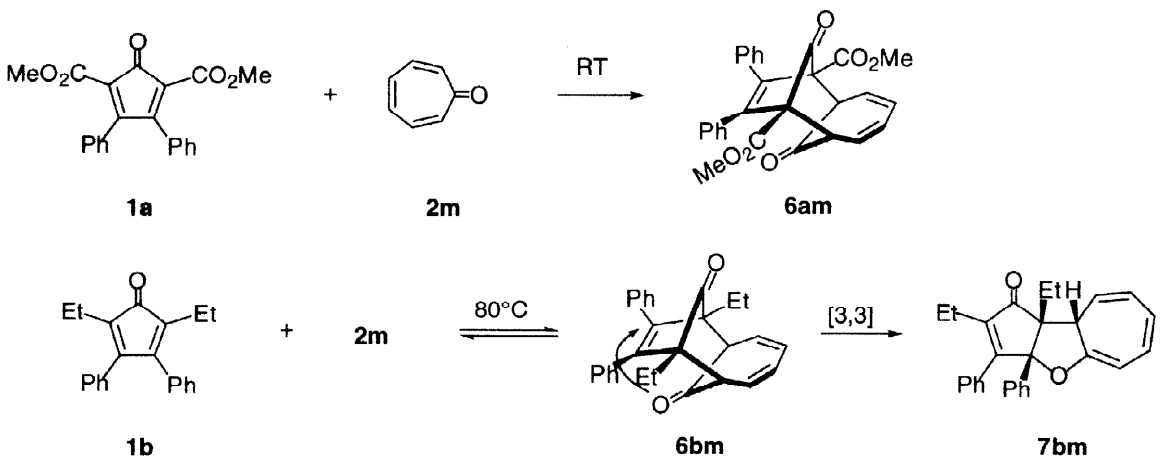
solvent	temp. (°C)	time (h)	yield (%)	**6af** :	**7af**
benzene	60°C	48	99	50 :	50
PCP	RT	96	96	98 :	2

Scheme 4

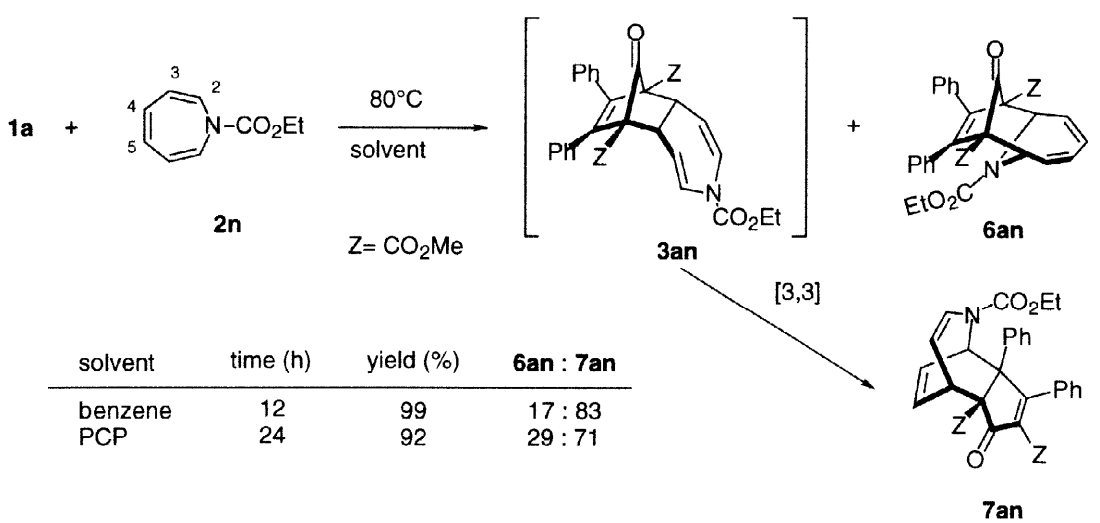
(**3af**).[11] When this reaction was carried out in PCP, the reaction was found to be about 15 times faster in PCP than in benzene. The effect of PCP on the periselectivity is worthy of note. The *endo* [4+2]π cycloaddition virtually disappeared at a sufficiently high concentration of PCP. The **6af**:**7af** ratio was 98:2 (total yield 96%).

The reaction behavior toward conjugated medium-ring polyenes having an electronegative functional group was quite different from that of **2f**.

The reaction of **1a** with tropone (**2m**) in benzene at room temperature gave the [4+6]π cycloadduct (**6am**) in 94 % yield.[8] When the reaction was carried out in PCP, a significant rate retardation was observed. The reaction reached an equilibrium point in which the ratio of **1a**:**6am** was 1:1.8.



solvent	time(h)	**6bm** :	**7bm** :	**1b**
benzene	8	59 :	29 :	12
PCP	20	9 :	91 :	0



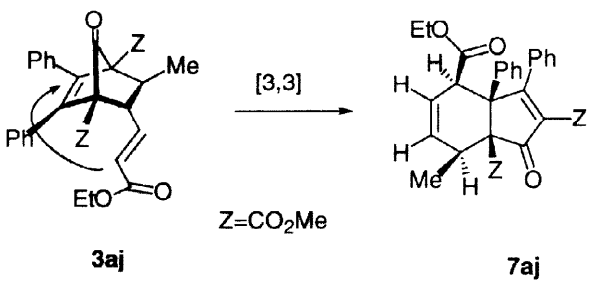
solvent	time (h)	yield (%)	**6an** : **7an**
benzene	12	99	17 : 83
PCP	24	92	29 : 71

Scheme 5

In connection with this reaction, the reaction behavior of 2,5-diethyl-3,4-diphenylcyclopentadienone (**1b**) was examined. The cycloaddition of **1b** with **2m** (5 eq) in benzene [8] afforded an equilibrium mixture of **6bm**, the [3,3]-sigmatropic rearrangement product (**7bm**) of **6bm** and the starting materials (Scheme 5). PCP hindered the cycloaddition, requiring a 2.5-fold longer reaction time in comparison with that in benzene. However, PCP enhanced the [3,3]-sigmatropic rearrangement of **6bm** to give **7bm**, *i.e.* the *endo*[2+8]π cycloadduct . When **6bm** was dissolved in PCP at 80°C, the immediate coloration was observed, indicating that PCP also enhanced the retro-[6+4]-cycloaddition reaction.

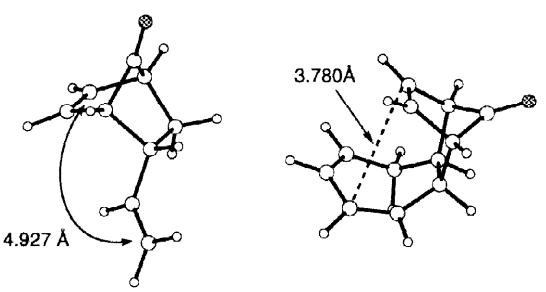
Next, the pericyclic reaction of **1a** with *N*-ethoxycarbonylazepine (**2n**) in PCP was investigated. The reaction in benzene at 80°C gave a 1:5 mixture of the *exo* [4+6]π cycloadduct (**6an**) and *endo* [2+4]π cycloadduct (**7an**).[12] The cycloadduct (**7an**) has been considered to be derived from the [3,3]-sigmatropic rearrangement of the *endo* [4+2]π cycloadduct (**3an**) (see Scheme 5). In PCP, the cycloaddition reaction was decelerated but the yield of the *exo* cycloadduct (**6an**) increased.

Pericyclic Reaction of Acyclic Conjugated Diene Heating a toluene solution of the cycloadduct (**3aj**) of **1a** and **2j** at 100°C for 24h gave the [3,3]-sigmatropic rearrangement product (**7aj**) in 33% yield. [10] In PCP, the yield of **7aj** increased to 64% even at 80°C for 8h (Scheme 6). In comparison with the [3,3]-sigmatropic rearrangement of the primary cycloadducts of conjugated medium-ring polyenes, the rearrangement of **3aj** seems to be geometrically unfavorable (see Scheme 6). However, PCP clearly accelerated the rearrangement rate.



3aj **7aj**

solvent	temp. (°C)	time (h)	yield (%)
toluene	100	24	33
PCP	80	8	64

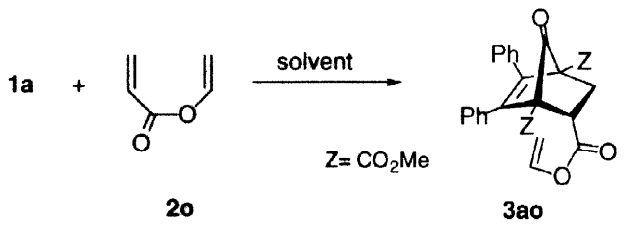


Ground-state structures of the model cycloadducts of cyclopentadienone with butadiene and cycloheptatriene.

Scheme 6

Cycloaddition with Dienophiles bearing Carbonyl or Hydroxy group In the cycloaddition with dienophiles bearing carbonyl or hydroxy group which can make hydrogen bond with phenols, the rate retardation was observed. For example, the rate for cycloaddition of **1a** with vinyl acrylate (**2o**) was 7.1-fold faster in benzene than in PCP (Scheme 7).

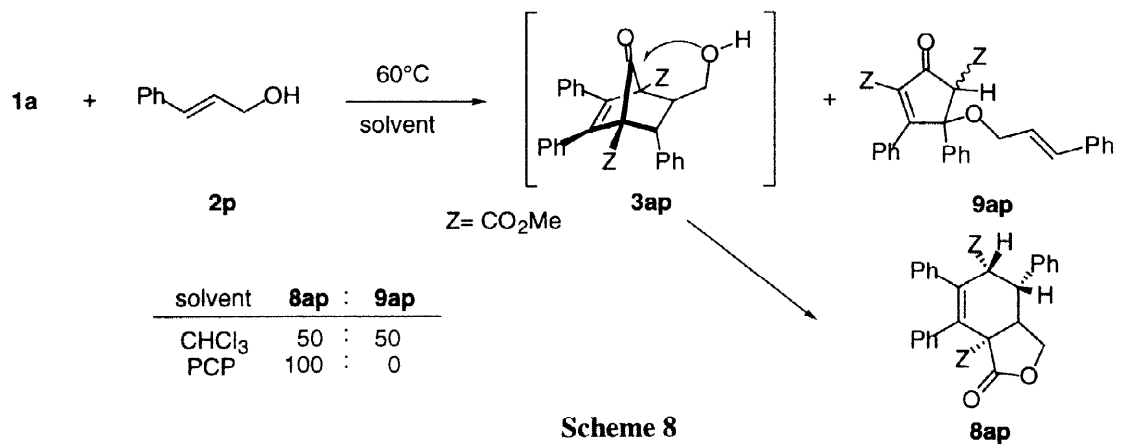
As mentioned above, similar rate retardation was observed in the cycloaddition of **1a** with **2m**. The pseudo first-order rate constants ($k_{benzene}$ and k_{PCP}) for benzene and PCP at 40°C are 5.46 x 10^{-4} and 0.057 x 10^{-4} sec^{-1}, respectively. The relative rate ($k_{PCP}/k_{benzene}$) is about 1/100.



solvent	$k \times 10^5(sec^{-1})$	$k_{benzene}/k_{PCP}$
benzene	170.78	7.1
PCP	24.13	

Scheme 7

Next, we examined the cycloaddition reaction of **1a** and cinnamyl alcohol (**2p**), in which the DA adduct (**3ap**) transformed to the corresponding phthalide derivative (**8ap**) [13] *via* intramolecular attack of the hydroxy group at the strained bridged carbonyl carbon of the DA adduct (Scheme 8). The ^{1}H-NMR and UV/Vis spectral studies [14] on the products derived from the reaction in benzene indicate that the 1,4-adduct (**9ap**) was produced (ca. 50% yield). The reaction in PCP resulted in exclusive formation of **3ap** which immediately transformed to **8ap**. Similar reaction behavior was observed in the cycloaddition of **1a** with allyl alcohol in PCP ($k_{toluene}/k_{PCP} = 4.1$).[15]



solvent	8ap : 9ap
$CHCl_3$	50 : 50
PCP	100 : 0

Scheme 8

Visible Absorption Spectra of ***1a,b*** *in PCP* The visible absorption (Vis) spectrum of **1b** in PCP showed a large blue shift of the n-π* absorption band of the carbonyl group.[16] The absorption band shifted from 448.4 nm to 416.8 nm on changing the solvent from benzene to PCP. In the case of **1a**, the n-π* absorption band could not be recognized because of the overlapping with the red-shifted π-π* absorption band.

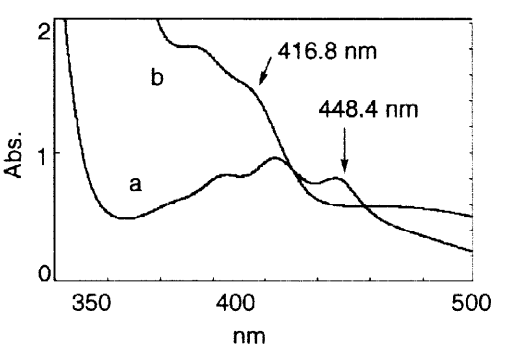


Figure 1. Visible Absorption Spectra of **1b** in benzene (a) and PCP (b).

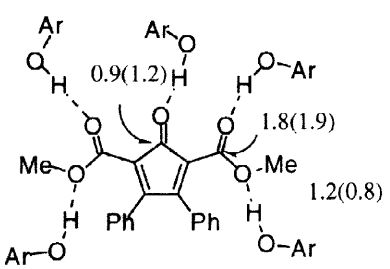
NMR Spectra of Complexes of 1a with Phenols To know the structure of the hydrogen-bonded **1a**, the NMR spectroscopic study was performed using PCP and *p*-nitrophenol (PNP). The shifts of the carbon chemical shifts of **1a** due to the hydrogen bonding to the oxygen atoms are summarized in Table 6.

Table 6. NMR Spectroscopic Data[a)] for **1a**, **1b**, **1a**+PNP, **1b**+PNP and **1a**+PCP.

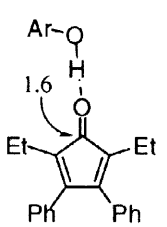
mole ratio of CP/Phenol's			^{1}H-NMR, δ [ppm]		^{13}C-NMR, δ [ppm]		
			-OH	-OMe	-OMe	ester C=O	enone C=O
1a	:	PNP[b)]					
1	:	0		3.72	51.6	161.9, 162.1	190.2
1	:	1		3.74	52.8	163.2, 163.9	191.1
1	:	3		3.75	53.0	163.5, 164.7	191.4
1	:	5		3.75	52.4	163.0, 164.0	191.4
1b	:	PNP[b)]					
1	:	0					203.6
1	:	1					205.2
1a	:	PCP[c)]					
1	:	0	5.24	3.73	51.6	161.9, 162.1	190.2
1	:	1	5.91	3.73	52.3	162.7, 163.3	191.0

a) Solvent $CDCl_3$. b) 400MHz c) 270MHz

The cyclopentadienone **1a** has five oxygen atoms to make hydrogen bond with phenols. The ^{13}C-NMR spectral data indicate that when a small amount of a phenol is used, the phenol forms hydrogen bonds with the ester carbonyl (1.9 ppm) and an increase of the phenol concentration causes exhaustive hydrogen bondings with the oxygen atoms.



1a



1b

Ar=$NO_2C_6H_4$

Figure 2. Chemical Shift Differences of **1a** and **1b** due to Complexation with PNP (1:1 mixture) . The shifts for the 1:5 mixture are given in parentheses.

Molecular Orbital Calculations To know the cycloaddition reactivity of cyclopentadienones, MO calculations on the parent cyclopentadienone (CP), **1a** and their PCP complexes [1:3 and 1:5 complexes (**1a**-3PCP and **1a**-5PCP)] were carried out using the PM3 method. [17a] The frontier molecular orbital (FMO) energies

and coefficients are summarized in Table 7. The LUMO energy level of **1a** is very low, indicating that **1a** participates in an inverse-type cycloaddition in Sustmann's classification for cycloadditions. [18] In actual reactions, as a large amount of PCP is used, all the oxygen atoms of **1a** are considered to form hydrogen bonds with PCP. The PM3 calculation indicates that hydrogen bonding of five molecules of PCP to **1a** (**1a**-5PCP) lowers the LUMO energy level by 0.73 eV, in which the difference in the LUMO coefficients of the reaction site (C_1 and C_4) between **1a** and **1a**-5PCP is small.

Table 7. FMO Energies and Coefficients of CP, CP-PCP, **1a**, **1a**-3PCP and **1a**-5PCP Calculated by PM3.[a)]

CP		CP-PCP		**1a**		**1a**-3PCP		**1a**-5PCP	
Orbital energies									
HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
-9.98	-1.10	-10.30	-1.50	-10.46	-1.72	-11.12	-2.41	-11.09	-2.45
Coefficients									
C_1 -0.566	0.418	C_1 0.566	-0.399	C_1 -0.460	0.417	C_1 0.536	-0.369	C_1 0.524	-0.393
C_2 -0.424	-0.412	C_2 0.420	0.414	C_2 -0.333	-0.428	C_2 0.379	0.396	C_2 0.356	0.439
		C_3 -0.425	0.409			C_3 -0.287	0.423	C_3 -0.375	0.435
		C_4 -0.568	-0.397			C_4 -0.411	-0.389	C_4 -0.558	-0.388

a) Energies are given in eV.

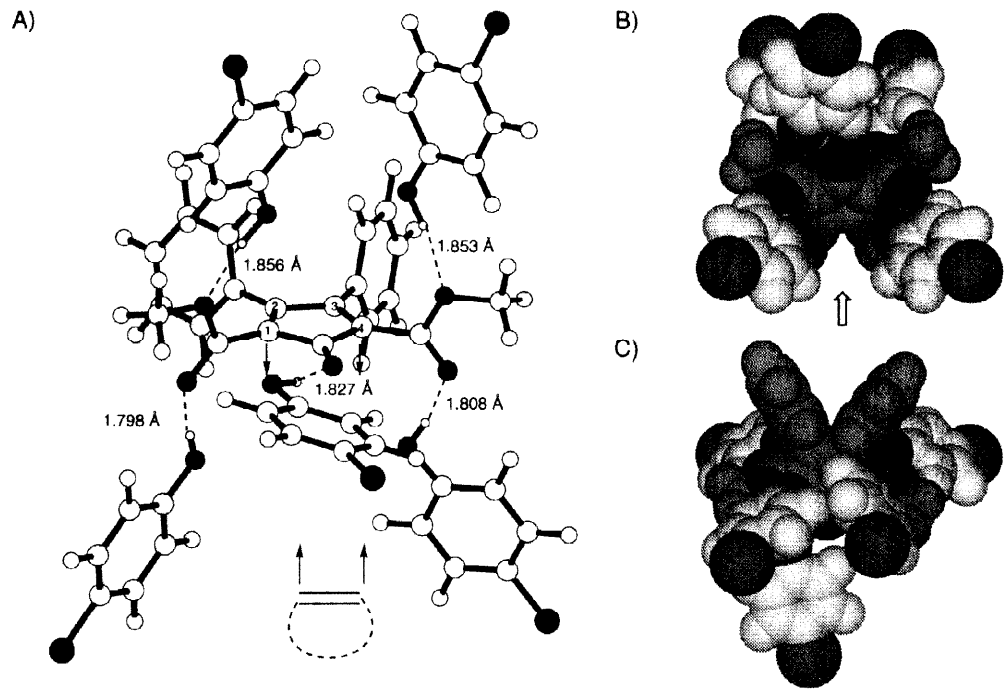


Figure 3. PM3-Optimized Structure of **1a**-5PCP. A) Hydrogen-bonded Geometry and Possible Access Direction of Dienophiles toward **1a**-5PCP. B) The Space Filling Model. C) The Backside View of B.

Figure 3 shows the fully optimized geometry of **1a**-5PCP. The distances of the five hydrogen bonds were calculated to range from 1.798 to 1.856 Å. The attack of dienophiles from the top is blocked by the two PCP

molecules hydrogen-bonded to the ether oxygen atoms. The approach of dienophiles is only allowed from the cavity formed by the three PCP molecules bonded to the three carbonyl oxygens.

To know the degree of TS stabilization due to the hydrogen bonding, the transition structures for the cycloaddition reactions of CP with ethylene in the presence of H_2O or PCP were calculated. The obtained heats of formation and reaction barriers are shown in Table 8 and the TS geometries are depicted in Figure 4. The forming C=C bond lengths are about 2.14 Å in every case.

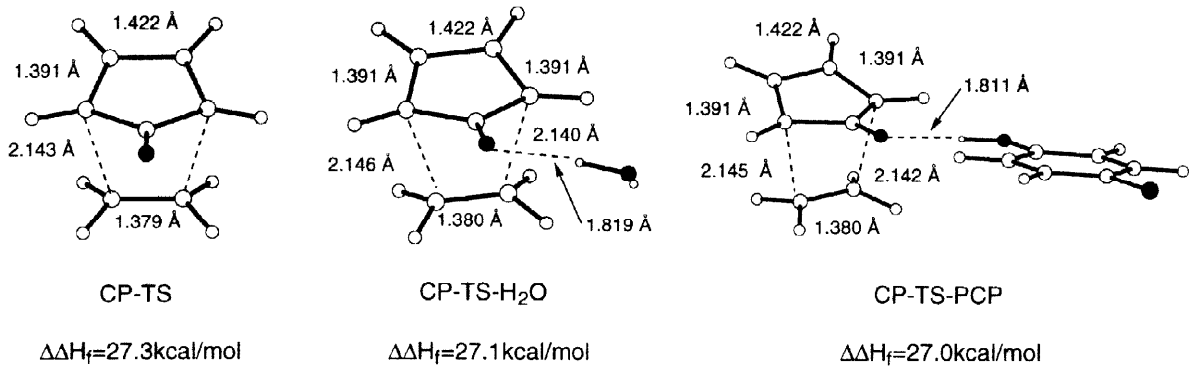


Figure 4. PM3-Calculated Transition Geometries and Reaction Barriers for Model Reactions of CP, CP-H_2O and CP-PCP with Ethylene.

Table 8. Heats of Formation of the Ground-state and Transition-state Structures for Model Reactions of CP, CP-H_2O and CP-PCP with Ethylene and the Ground-state Structures of **1a**, **1a**-3PCP and **1a**-5PCP Calculated by PM3.

Geometry		ΔH_f[a)]	Geometry		ΔH_f[a)]	$\Delta\Delta H_f$[b)]
GS	**1a**	-97.8	GS	**1a**-5PCP	-256.5	
	CP	10.6		CP-H_2O	-45.8	
	ethylene	16.6		CP-PCP	-21.3	
	PCP	-28.4	TS	CP-TS	54.5	27.3
	H_2O	-53.4		CP-TS-H_2O	-2.1	27.1
	1a-3PCP	-194.5		CP-TS-PCP	22.3	27.0

a) kcal/mol. b) $\Delta\Delta H_f = \Delta H_f^{TS} - \Delta H_f^{GS}$.

Discussion

The UV/Vis absorption and NMR spectral data indicate that phenols make hydrogen bonds with the carbonyl oxygen atoms of cyclopentadienones. The visible absorption spectrum of **1b** in PCP showed a sizable blue shift (31.6 nm), which corresponds to the stabilization of the ground state (GS) by 5.2 kcal/mol.[19] In the cycloaddition of cyclopentadienones with nonactivated olefins, the rate enhancement was observed although the ground state is stabilized by the hydrogen bonding. This suggests that the transition state is more effectively stabilized than the ground state by PCP. As stated above, the activation entropies for **1a** in benzene and PCP are -35 and -36 e.u., respectively, indicating that the difference of freedom of motion between the ground state and the transition state in PCP is almost the same as that in benzene. In the transition state, PCP probably still forms hydrogen bonds with **1a** in the same way as in the ground state. From these observations, the cycloaddition reactivity is considered to depend upon the enthalpy of activation.

Inspection of the heats of formation (ΔH_f) of the model cycloadditions of CP and CP-PCP with ethylene indicates (see Figure 4) that the reaction barrier ($\Delta\Delta H_f$) in PCP is about 0.3 kcal/mol less than that without PCP, in accordance with the trend observed in the reactions of **1a** in benzene and PCP.

The PM3 calculations indicate that the LUMO energy level of CP is stabilized from -1.10 eV to -1.50 eV by the hydrogen bonding with PCP and the LUMO energy levels of **1a**, **1a**-3PCP and **1a**-5PCP are -1.72eV, -2.41eV and -2.45eV, respectively. (see Table 7) The hydrogen bonding to the ester carbonyls plays an important role to lower the LUMO energy.

At least in the cycloaddition with nonactivated olefins, the lowering of the LUMO energy of the cyclopentadienones seems to be a main contributor to the rate enhancement. As can be seen in Table 2, any dienophile having a higher HOMO energy level seems to be effectively affected by PCP, supporting that the cyclopentadienones act as acceptors in the inverse-type cycloaddition. When a large excess of PCP is used in the cycloaddition, PCP would form hydrogen bonds with all the oxygen atoms of **1a**. Inspection of the most stable ground-state geometry of **1a**-5PCP indicates that the motions of the COOMe groups are unduly restricted by addition of PCP. In such a situation, the direction of the access of dienophiles is assumed to be strictly controlled. As deduced from the van der Waals dot surface, dienophiles probably attack **1a** from a less hindered *exo* site, resulting in the predominant formation of the *exo* DA adducts (see Figure 3).

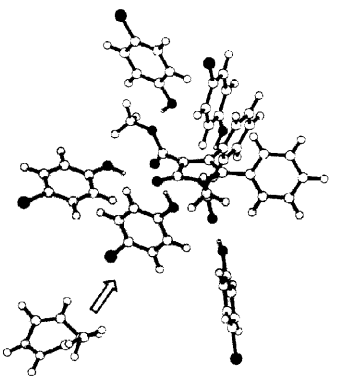


Figure 5. Periselective Attack of **2f** toward **1a**-5PCP.

Similar cycloaddition behavior was found in the pericyclic reaction of **1a** with **2f** in which the use of PCP dramatically changed its periselectivity to bring about the predominant formation of the *exo* [4+6]π cycloadduct (see Figure 5 and Scheme 4).

As mentioned above, in the cycloaddition with dienophiles having carbonyl or hydroxy group which can make hydrogen bonds with phenols, a significant rate retardation was observed in every case. These may be due to large steric interference between the sterically crowded cyclopentadienone-PCP and dienophile-PCP complexes.

These observations indicate that the complexation of phenols with cyclopentadienones by hydrogen bonding plays a leading role in determination of the *endo/exo* and periselectivities.

The origin of the rate enhancement for the decarbonylation and [3,3]-sigmatropic rearrangement reactions may be due to the hydrogen bonding [3a, 20] between phenols and the carbonyl group of the strained bicyclo[2.2.1]hept-2-en-7-one moiety of the primary DA adducts. In FMO viewpoint, the observed rate enhancements for decarbonylation and [3,3]-sigmatropic rearrangement may be interpreted in terms of the favorable three system interaction, [12, 21] in which the LUMO energies of the breaking σ-bonds are lowered by the hydrogen bonding with phenols (see Figure 6).

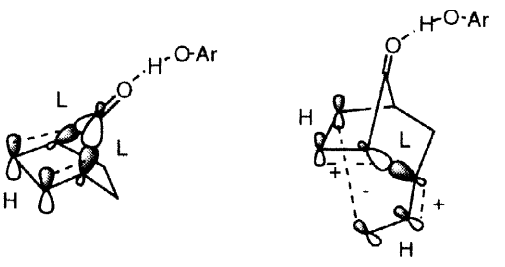


Figure 6. Three System Interactions for Decarbonylation and [3,3]-Sigmatropic Rearrangement.

Phenols other than PCP showed similar solvent effects. Of liquid phenols studied, PCP showed very interesting solvent effects on pericyclic reactions of various types.

In conclusion, phenols are interesting solvents for the cycloaddition reaction of cyclopentadienones with nonactivated olefins. The lowering of the LUMO energy of cyclopentadienone plays a leading role in determination of the cycloaddition reactivity and the steric interference

between the phenol-cyclopentadienone and dienophiles controls the peri- and *endo/exo* selectivities.

Experimental

The melting points were uncorrected. The IR spectra were taken with a Hitachi 270-30 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were taken with JEOL JNM-EX 270 (270 MHz), GX-400 (400 MHz) and JNM-A 500 (500 MHz) spectrometers for ca.10% solution with TMS as an internal standard; chemical shifts are expressed as δ values and the coupling constants (*J*) are expressed in Hz. UV/Vis spectra were recorded on a Simadzu UV-2500PC spectrophotometer.

Materials .- 2,5-*Bis*(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) [22] and 2,5-diethyl-3,4-diphenyl-cyclopentadienone (**1b**) [23] were prepared according to the previously reported methods. Compounds **3ae**, **5ae**, **3ab**, **3aj**, **3al**, **5ab**, **5aj**, **5al**, **6af**, **7af**, **6am**, **6bm**, **7bm**, **6an**, **7an**, **7aj**, **3ao**, **8ap** and **9ap** were previously reported by one of the authors of this papers.[5, 7-12]

*Cycloadditions of **1a**, **1b** with Dienophiles in Benzene (General Procedure).*- The procedure was similar to that described in the previous papers.[5, 7-12] A mixture of **1a** or **1b** (2.8 - 5.7 x 10^{-4} mol) and an excess amount of a dienophile (6 -15 x 10^{-4} mol) in a solvent was stirred at a given temperature until the red color faded away (see Schemes 2-8 for reaction conditions). The solvent was evaporated under reduced pressure. The residual oil was treated with methanol to give a solid. The crude product was purified by recrystallization from EtOH or chromatography on silica gel. The formation ratio was determined by 270 MHz ^{1}H-NMR spectroscopy.

The known compounds (**3ae**, **3ab**, **3aj**, **3al**, **6af**, **7af**, **6am**, **6bm**, **7bm**, **6an**, **7an**, **3ao**, **8ap** and **9ap**) were identified by comparison of the ^{1}H-NMR spectra with those of authentic samples.

Cycloadduct **3ak** was obtained as colorless prisms: mp 114-115°C (from MeOH); IR (KBr) cm^{-1}: 1794 (bridge C=O), 1730 (ester C=O); ^{1}H-NMR (500MHz, $CDCl_3$) δ : 1.64 (1H, dd, *J* = 6, 13 Hz, methylene-*endo*), 1.98 (1H, m, methylene), 2.78 (1H, dd, *J* =9, 13 Hz, methylene-*exo*), 2.88-3.00 (1H, m, methylene), 3.06 (1H, dt, *J* = 9, 6 Hz, methine), 3.63 and 3.64 (6H, s, -OMe), 5.13 (2H, q, *J* =15 Hz, CH_2-CH=C*H*$_2$), 5.86-5.78 (1H, m, CH_2-C*H*=CH_2), 7.26-7.08 (10H, m, ar); ^{13}C-NMR (125MHz,$CDCl_3$) δ : 32.1 (methylene), 37.0 (methine), 37.7 (methylene), 52.2 (-OMe), 64.8 and 68.4 (s), 117.5 (olefinic methylene), 127.8, 128.1, 128.2, 128.5, 128.9 and 129.0 (ar), 133.3, 133.6, 137.5 and 140.2 (s), 134.5 (olefinic methine), 167.4 and 167.8 (>C=O), 191.2 (bridge >C=O); MS (m/z) 416 (M^+) . Anal. Calcd for $C_{29}H_{28}O_7$: C, 71.30, H, 5.78. Found:C, 70.77, H, 5.83 %.

*Cycloadditions of **1a** with Some Dienophiles in PCP (General Procedure).*- A solution of **1a** (2.8-5.7 x 10^{-4} mol) with an excess amount of a diene (6-15 x 10^{-4} mol) in PCP was stirred at given temperature until the red color faded away (see Schemes 2-8 for reaction conditions). The mixture was diluted with benzene and washed three times with 10% sodium hydroxide. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The cycloadduct was isolated as a mixture of the stereoisomers and its formation ratio was determined by 270 MHz ^{1}H-NMR spectroscopy.

*Cycloadditions of **1a** with **2f** in PCP.*- A solution of **1a** (0.20 g, 5.7 x 10^{-4} mol) and **2f** (0.12 ml, 14.7 x 10^{-4} mol) in PCP (1 ml) was stirred at room temperature for 96 h. The mixture was diluted with benzene and washed three times with 10 % sodium hydroxide. The organic layer was dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to give the mixture of cycloadducts **6af** and **7af**. The formation ratio (**6af** : **7af**) is 98 : 2. The resulting solid was recrystallized from EtOH to give **6af** as colorless prisms.

The minor cycloadduct **7af** was identified by comparison of the ^{1}H-NMR spectrum with that of the adduct isolated in benzene.

*Cycloadditions of **1a** with **2e** in PCP.*- The procedure was similar to that described in the previous paper.[7]

The known compound (**5ae**) was identified by comparison of the ^{1}H-NMR spectrum with that of an authentic sample. A solution of **1a** (0.50 g, 1.4 x 10^{-3} mol) and **2e** (1.52 g, 14.1 x 10^{-3} mol) in PCP (2 ml) was stirred at 120 °C for 12 h. The mixture was diluted with benzene and washed three times with 10 % sodium hydroxide. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The resulting oil was purified by chromatography on silica gel with AcOEt-benzene (1:20) to give **5ae** as colorless prisms

*Thermolyses of the [4+2]π Cycloadduct (3ae, ab, aj-al). Formation of DDA Adduct (**5ae, ab, aj-al**).*- The procedure was similar to that described in the previous paper. [9] The known compounds (**5ab**, **5aj** and **5al**) were identified by comparison of the ^{1}H-NMR spectra with those of authentic samples. The [4+2]π adduct (**3ae**, 0.50 g) was heated at 170°C to give oil with evolution of CO gas. The oily mass was purified by chromatography on silica gel using AcOEt-benzene (1:20) as an eluent to give the pure sample of DDA adduct (**5ae**). Similarly, **3ab**, **aj-al** gave **5ab**, **aj-al**, respectively.

Compound **5ak** was obtained as colorless needles: mp 129-130°C (from EtOH) ; IR (KBr)cm^{-1}: 1726 (>C=O); ^{1}H-NMR (500MHz, $CDCl_3$) δ : 1.07 (1H, d, J =10 Hz, methylene), 2.03- 2.05 (2H, m, methylene), 2.19 (H, d, J =13 Hz, methylene), 2.83-2.85 (2H, t, J = 7 Hz, methine), 3.22 and 3.27 (6H, s, -OMe), 6.86-7.26 (10H, m, ar); ^{13}C-NMR (125MHz,$CDCl_3$) δ : 36.7 and 36.8 (methylene), 38.1 (methine), 51.3 and 51.5 (-OMe), 52.1 and 57.1 (s), 126.2, 126.5, 127.2, 127.5, 127.8, 128.4, 129.0 and 129.6 (ar), 134.9, 135.6, 141.7 and 147.0 (s), 175.1 and 174.9 (>C=O); MS (m/z) 388 (M^+). ; *Anal.* Calcd. for $C_{25}H_{24}O_4$: C, 77.30, H, 6.23. Found: C, 77.25, H, 6.24.

*Thermolyses of the [4+2]π Cycloadduct (**3ab, aj-al**). Formation of DDA Adduct (**5ab, aj-al**) in PCP.*- A solution of **3ab** (0.50g) in PCP (2ml) was heated at 100°C for 24h. The mixture was diluted with benzene and washed three times with 10% sodium hydroxide. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure.The residual oil was purified by chromatography on silica gel using AcOEt-benzene (1:20) as an eluent to give **5ab**. Similarly, **3aj-al** gave **5aj-al**, respectively.

*[3,3]-Sigmatropic Rearrangement of Endo [4+2]π Cycloadduct (**3aj**) to Endo [2+4]π Cycloadduct (**7aj**).* - The procedure was similar to that described in the previous paper.[10] The known compound (**7aj**) was identified by comparison of the ^{1}H-NMR spectrum with that of an authentic sample. A solution of **3aj** (0.50g) in toluene (2ml) was heated at 100°C for 24h. The solvent was evaporated under reduced pressure. The residual oil was purified by chromatography on silica gel using AcOEt-benzene (1:20) as an eluent to give **7aj**.

*[3,3]-Sigmatropic Rearrangement of Endo [4+2]π Cycloadduct (**3aj**) to Endo [2+4]π Cycloadduct (**7aj**) in PCP.*- A solution of **3aj** (0.50g) in PCP (2ml) was heated at 80°C for 8h. The mixture was diluted with benzene and washed three times with 10% sodium hydroxide. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residual oil was purified by chromatography on silica gel using AcOEt-benzene (1:20) as an eluent to give **7aj**.

Kinetics .- The pseudo-first-order conditions were maintained by using a 100:1 ratio of dienophiles to **1a** in benzene, PCP or benzene-phenol mixtures. The rates were followed at 40.0 ± 0.1 °C by measuring the decrease of the absorption at 430 (benzene) or 490 nm (PCP), using a 10 mm quartz cell sealed with a ground-glass stopper. The pseudo-first-order rate constants were determined by using infinity values taken after 10 half-lives. The results are listed in Tables 2, 3, 4 and 9.

Molecular Orbital Calculation.- Semiempirical SCF-MO calculations were run through the ANCHOR II interface using MOPAC-V6.0 [17b] on a Fujitsu S4/2 work station (WS) or through the CS Chem3D Pro interface using MOPAC93 on a Macintosh G3 personal computer. The computations of **1a**, **1a**-3PCP and **1a**-5PCP were

carried out on a Scientists' Paradise Dragon AXP5A/433 computer. The transition structures were obtained using the TS keyword and characterized by the presence of a single negative Hessian eigenvalue. Graphical analysis of the MO calculation data was performed on a Macintosh G3 or 8500/150 personal computer.

The structure of **1a**-3PCP and **1a**-5PCP was obtained using a starting geometry in which all the substituents were rotated by 90° out of the plane of cyclopentadienone.

Structure of **1a**-3PCP: The optimized geometry shows that the distances of the hydrogen bonds between C1C=O--HO-Ar, C2C=O--HOAr and C5C=O--HOAr are 1.827, 1.815 and 1.813 Å, respectively, and the dihedral angles of C1-C2-C=O, C2-C3-C_{Ar}=C_{Ar}, C5-C4-C_{Ar}=C_{Ar} and C1-C5-C=O are -97.7, 80.8, -128.4 and 98.2°, respectively. The optimized geometry is independent of the input geometries.

Structure of **1a**-5PCP: The optimized geometry shows that the distances of the hydrogen bonds between C1C=O--HO-Ar, C2C=O--HOAr C2C=O-O--HOAr, C5C=O--HOAr and C5C=O-O--HOAr are 1.827, 1.798, 1.865, 1.808 and 1.853 Å, respectively, and the dihedral angles of C1-C2-C=O, C2-C3-C_{Ar}=C_{Ar}, C5-C4-C_{Ar}=C_{Ar} and C1-C5-C=O are -97.5, 84.2, -71.0 and -98.3°, respectively.

Table 9. Pseudo-first-order Rate Constants (k) for the Reaction of **1a** with **2c** in Benzene and PCP at Different Temperatures.

solvent	temp. (°C)	k x10^3 (sec^{-1})	solvent	temp. (°C)	k x10^3 (sec^{-1})
benzene	25.0	0.744	PCP	43.0	16.53
	30.0	1.024		46.0	19.14
	35.0	1.399		49.0	22.12
	40.0	1.935		52.0	26.17

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