hydrochloric acid. The aromatic carboxylic acid formed was extracted three times with ether. Removal of ether and acetic acid under reduced pressure gave the pure acid.

In the case of 4′-carboxybenzo-15-crown-5, this procedure gave crude acid contaminated with hexafluorophosphate ion. Pure 4′-carboxybenzo-15-crown-5 was obtained by washing three times with hot dilute hydrochloric acid.

Carboxylation with Bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$). A reaction mixture of diazonium salts and sodium acetate in an appropriate solvent was cooled with a dry ice–methanol bath. $Pd(dba)_2$ was added to the reaction mixture. After the introduction of 9 kg/cm^2 of carbon monoxide, the reaction mixture was warmed to room temperature and stirred for 1 h. After that, the same procedure was employed as that described above.

Carboalkoxylation of Arenediazonium Salts. Almost the same procedure as that described above was employed before workup. The reaction mixture was treated with aqueous sodium bicarbonate and extracted with ether. The aqueous layer gave benzoic acid after acidification. The organic layer was distilled under reduced pressure. The distillate was analyzed by NMR and GLC.

Registry No. Benzenediazonium tetrafluoroborate, 369-57-3; 4-methylbenzenediazonium tetrafluoroborate, 459-44-9; 3-methylbenzenediazonium tetrafluoroborate, 1422-76-0; 2-methylbenzenediazonium tetrafluoroborate, 2093-46-1; 2,6-dimethylbenzenediazonium tetrafluoroborate, 2192-33-8; 4-methoxybenzenediazonium tetrafluoroborate, 18424-07-2; 4-chlorobenzenediazonium tetrafluoroborate, 673-41-6; 3-chlorobenzenediazonium tetrafluoroborate, 14874-10-3; 2-chlorobenzenediazonium tetrafluoroborate, 1956-97-4; 4-bromobenzenediazonium tetrafluoroborate, 673-40-5; 4-iodobenzenediazonium tetrafluoroborate, 1514-50-7; 2-iodobenzenediazonium tetrafluoroborate, 7169-58-6; 4-nitrobenzenediazonium tetrafluoroborate, 456-27-9; 1-naphthalenediazonium tetrafluoroborate, 318-50-3; 4′-benzo-15-crown-5-diazonium hexafluorophosphate, 73368-13-5; methanol, 67-56-1; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; butanol, 71-36-3; benzoic acid, 65-85-0; 4-methylbenzoic acid, 99-94-5; 3-methylbenzoic acid, 99-04-7; 2-methylbenzoic acid, 118-90-1; 2,6-dimethylbenzoic acid, 632-46-2; 4-methoxybenzoic acid, 100-09-4; 4-chlorobenzoic acid, 74-11-3; 3-chlorobenzoic acid, 535-80-8; 2-chlorobenzoic acid, 118-91-2; 4-bromobenzoic acid, 586-76-5; 4-iodobenzoic acid, 619-58-9; 2-iodobenzoic acid, 88-67-5; 4-nitrobenzoic acid, 62-23-7; 1-naphthoic acid, 86-55-5; 4′-benzo-15-crown-5-carboxylic acid, 56683-55-7; 2,6-dimethylbenzoic anhydride, 73368-14-6; aceto-2,6-dimethylanilide, 2198-53-0; methyl 4-iodobenzoate, 619-44-3; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; *tert*-butyl benzoate, 98-06-6; benzoic anhydride, 93-97-0; butyl benzoate, 136-60-7; benzoic 1-naphthoic anhydride, 73368-15-7; $Pd(dba)_2$, 32005-36-0; Li_2PdCl_4, 15525-45-8; $Pd(OAc)_2$, 33571-36-7.

Frontier-Controlled Pericyclic Reaction of Phencyclone with 1*H*-Azepine. Remarkably Accelerated Aromatic Cope Rearrangement of an Endo-[4 + 2]-π Cycloadduct

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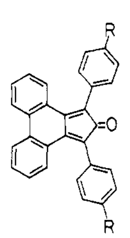
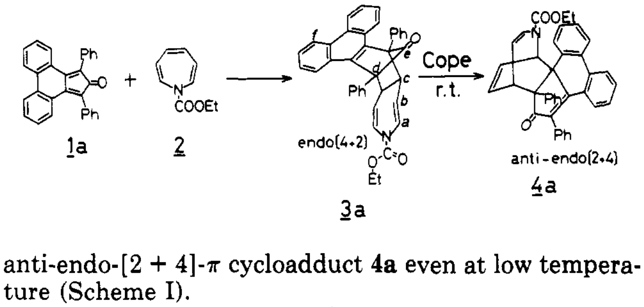
The endo-[4 + 2]-π cycloadducts of phencyclone derivatives and *N*-(ethoxycarbonyl)azepine were isolated and readily isomerized to anti-endo-[2 + 4]-π cycloadducts. The kinetics of the rearrangement of endo-[4 + 2]-π cycloadducts have been examined. The aromatic Cope rearrangement showed a first-order process with relatively low sensitivity to the ionizing power of the medium, indicating that it proceeds by a mechanism which involves very little change in charge separation between the ground state and the transition state. The rearrangement rates of endo-[4 + 2]-π cycloadducts to anti-endo-[2 + 4]-π cycloadducts were affected by changing the 2,5-substituents of the cyclopentadienones. The results can be explained in terms of the three-system interaction theory.

During the course of a study on the pericyclic reaction of phencyclone (**1a**)[1] with *N*-(ethoxycarbonyl)azepine (**2**), we have found that the endo-[4 + 2]-π cycloadduct **3a** readily undergoes aromatic Cope rearrangement to the anti-endo-[2 + 4]-π cycloadduct **4a** even at low temperature (Scheme I).



1a : R = H
1b : R = Cl
1c : R = OCH_3

Scheme I



The Cope rearrangement does not readily occur if one double bond of the 1,5-hexadiene system is incorporated in an aromatic ring. Recently, Marvell and Lin[2] demonstrated the first example of an aromatic Cope rearrangement by introducing a cyclopropane ring into the 4-

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(1) (a) Part 3 of this series. Presented in part at the 12th Congress of Heterocyclic Chemistry, Tokyo, Japan, October 24, 1979. (b) Part 2: Yasuda, M.; Harano, K.; Kanematsu, K., *J. Org. Chem.* 1980, *45*, 659–64.

(2) Marvell, E. N.; Lin, C., *J. Am. Chem. Soc.* 1978, *100*, 877–83, and references cited therein.

0022-3263/80/1945-2368$01.00/0

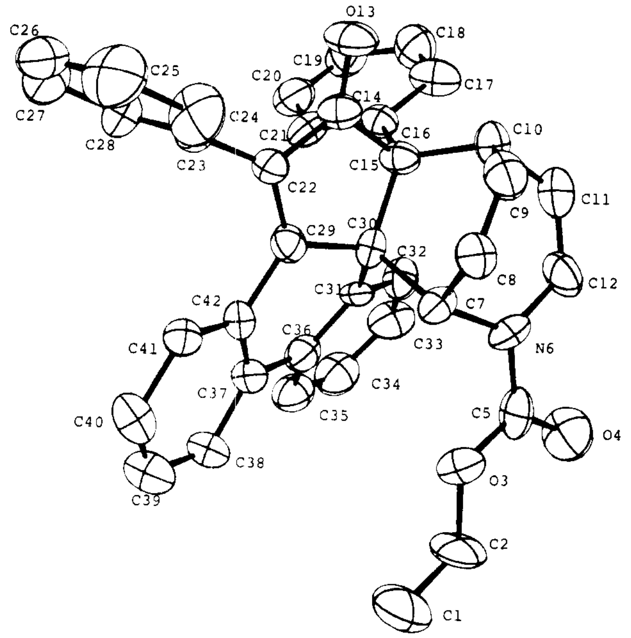

Figure 1. ORTEP drawing of anti-endo-[2 + 4]-π cycloadduct **4a**.

phenyl-1-butene system and heating at 121 °C for 20 h. The loss of aromatic resonance energy was compensated for by the relief of strain accompanying opening of the cyclopropane ring.

We now discuss the rearrangement of endo-[4 + 2]-π cycloadducts **3** based on the kinetic data.

Results and Discussion

Phencyclone derivatives (**1**, 1 mol) and a slight excess of *N*-(ethoxycarbonyl)azepine (**2**, 4 mol) reacted at room temperature to give 1:1 cycloadducts **3** in high yields. The spectral data of these structures (**3a–c**) grossly resemble each other. The NMR spectrum of the adduct **3a** exhibited two bridgehead protons as a doublet ($J = 4$ Hz) at δ 4.16, two vinyl protons β to nitrogen as a double doublet ($J = 10$ Hz) at δ 5.32, and two vinyl protons α to nitrogen as a doublet at δ 6.20. The symmetry of the molecule was apparent. Comparison of the NMR spectra of **3a** and an analogous cycloadduct (**5**) of 2,5-dimethyl-3,4-diphenylcyclopentadienone with **2** revealed that the protons α to the nitrogen of **3a** have undergone an upfield shift relative to those of **5**.[3] This fact indicates the existence of the phenanthrene ring-current effect on the protons α to the nitrogen, suggesting the endo-[4 + 2]-π structure for **3a**. Further, the IR spectrum of **3a** indicated the presence of a strained bridged carbonyl group (1786 cm^{-1}), a urethane carbonyl function (1730 cm^{-1}), and the vinyl group adjacent to the urethane moiety (1682 cm^{-1}).

On the other hand, **1a** and **2** reacted at 80 °C to give the anti-endo-[2 + 4]-π cycloadduct **4a**[4] in high yield. The ^{1}H and ^{13}C NMR spectra of **4a** were difficult to analyze precisely because of the large number of overlapping resonances. An X-ray crystallographic study was carried out in order to elucidate the molecular structure of **4a**. The crystal structure was solved by the direct method. Refinement to an *R* factor of 6.8% was obtained by the method of least-squares on 1927 nonzero structure factors. As can be seen in the computer-generated drawing[5] (Figure 1), adduct **4a** is established to be an anti-endo-[2 + 4]-π cycloadduct wherein the carbonyl group is oriented anti to the urethane group. The framework of **4a**, which consists of 1*H*-azepine and cyclopentadienone moieties, is strained considerably. Interbond angles at sp^2 carbons [C_7–C_8–C_9 117.4°, C_6–C_{12}–C_{11} 126.5°, and C_{10}–C_{11}–C_{12} 125.0°] deviate by 2.6°, 3.5°, and 5.0°, respectively, from the unstrained angles of 120°. The sp^3 carbons suffer similar deviations from the tetrahedral angles of 109.5°. The C_7–C_{30} and C_{15}–C_{30} bond lengths, 1.58 Å and 1.57 Å, respectively, are considerably longer than the usual value of 1.54 Å. These unusually long bond distances might be caused by large steric repulsions between the 1*H*-azepine moiety and the phenanthrene moiety of phencyclone (**1a**). N_6 deviates by 0.07 Å from the plane of the three atoms bound to it, indicating sp^2 hybridization. The N_6–C_{12} bond (1.40 Å) is shorter than the accepted value for N–C single bonds, e.g., the N_6–C_7 bond (1.48 Å). The torsional angle of O_4–C_5–N_6–C_{12} is 2.73°. These facts suggest that O_4, C_5, N_6, C_{12}, C_{11}, C_{10}, and C_7 are roughly planar, forming a resonance structure of the vinyl urethane, and support the IR and UV spectral data described above. The dihedral angle between the two phenyl rings of the biphenyl moiety is 17.8°.

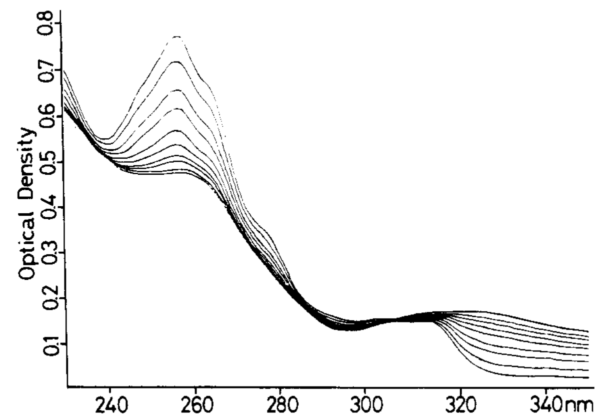

Figure 2. UV spectral change with the lapse of time for the rearrangement of endo-[4 + 2]-π cycloadduct **3a** in ethanol at 34.1 ± 0.1 °C.

Table I. Rate Constants (k_1) for Rearrangement of 3a in Various Solvents at 47.8 ± 0.1 °C

solvent	E_T, kcal mol^{-1} (25 °C)	$k_1 \times 10^5$, s^{-1}
$(CH_2OH)_2$	56.3	72.4
C_2H_5OH	51.9	24.2
$CH_3(CH_2)_2CH_2OH$	50.2	28.1
CH_3CN	46.0	4.73
$(CH_3)_3COH$	43.9	14.6
$(CH_3)_2NCOH$	43.8	7.88
C_6H_5CN	42.0	6.57
$(CH_3)_2NCON(CH_3)_2$	41.0	5.51
C_6H_5Cl	37.5	3.79

Figure 2 shows the UV spectral change as a function of time upon heating the cycloadduct **3a** in ethanol at 34.1 °C; the absorption at 253 nm due to a vinyl urethane moiety decreases with the increase of that at 330 nm due to an enone conjugated with two phenyl groups. The UV spectrum agreed with that of **4a**[3] after the solution was allowed to stand at 34.1 °C for about 10 half-lives. The rate of reaction was determined by measuring the increase of the absorbance at 330 nm. In this solvent, satisfactory

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[3] Paquette, L. A.; Kuhla, D. E.; Barrett, J. H.; Leichter, L. M., *J. Org. Chem.* **1969**, *34*, 2888–96.

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Table II. Rearrangement Rate Constants and Activation Parameters of 3 at Various Temperatures

compd	solvent	temp, °C	$k_1 \times 10^5$, s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu[a]
3a	C_2H_5OH	34.1	4.99	25.6	2.71
		40.0	7.49		
		47.8	24.2		
		58.9	104		
	C_6H_5Cl	34.1	0.52	27.5	4.75
		40.0	1.34		
		47.8	3.79		
		58.9	15.4		
3b	C_2H_5OH	47.8	44.6		
3c	C_2H_5OH	47.8	23.4		

[a] Calculated from the value obtained at 47.8 °C by making the usual assumption that the transmission coefficient (κ) equals unity.

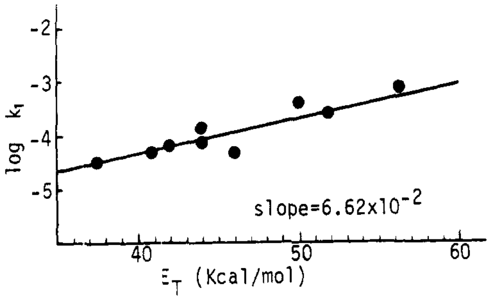

Figure 3. Plot of log k_1 vs. E_T for the rearrangement.

first-order behavior of the reaction was observed; it was also the same in other solvents (see Table I). The rate constants at various temperatures and the activation parameters calculated in the usual manner are summarized in Table II. The E_T values of Dimroth,[6] based on the bands of solvatochromism of pyridinium N-phenylbetaines, were used as a scale of solvent ionizing power in studying the effect of solvent on the rate of rearrangement, because they were obtained with a wider variety of solvents than the other known scales.[7-9] As illustrated in Figure 3, plots of log k_1 vs. E_T values for **3a** show a linear relationship (log $k_1 = aE_T + b$). Values of the least-squares slope a are summarized in Table III.[10] As shown in Table III, a = 40.4 × 10^{-2} for the rearrangement of 2-(diethylamino)ethyl S-methyl xanthate to the corresponding S,S-dialkyl dithiocarbonate, a = 31.2 × 10^{-2} for the pyrolysis of benzhydryl S-phenyl thiocarbonate to the sulfide, and a = 29.1 × 10^{-2} for the allylic rearrangement of *cis*-5-methyl-2-cyclohexenyl acid phthalate. These values are very large, indicating that the rearrangement reactions occur through highly polarized transition states such as the ion pair which has been previously proposed with some evidence.[11-13] On the other hand, a in the case of **3a** is small and comparable to the value in the case of allyl

Table III. Sensitivity of Various Reactions to Solvent Ionizing Power (E_T Value)

substrate	solvent sensitivity parameter, $a^a \times 10^2$
2-(diethylamino)ethyl S-methyl xanthate[b]	40.4[e]
benzhydryl S-phenyl thiocarbonate[c]	31.2[f]
cis-5-methyl-2-cyclohexenyl acid phthalate[b,d]	29.1[f]
p-methoxyneophyl p-toluenesulfonate[b]	17.9[e]
α-methylallyl chloroformate[d]	17.6[f]
1-phenylallyl 3,4,5-tribromobenzoate[d]	13.5[e]
2,2,2-triphenylethyl S-methyl xanthate[c]	12.8[f]
cinnamyl S-methyl xanthate[d]	12.6[e]
2,2-diphenylpropyl S-methyl xanthate[c]	10.9[f]
α-phenethyl chloroglyoxalate[c]	10.2[f]
α-trifluoromethylallyl chlorosulfinate[d]	7.60[f]
endo-[4 + 2]-π cycloadduct **3a**[d]	6.62
allyl S-methyl xanthate[d]	6.46[e]
neophyl S-methyl xanthate[c]	5.90[f]
allyl p-cresyl ether[d]	4.34[g]
allyl thiobenzoate[d]	4.24[e]

[a] log $k_1 = aE_T + b$. [b] Solvolysis. [c] Pyrolysis. [d] [3,3]-Sigmatropic rearrangement. [e] See ref 10a. [f] See ref 10b. [g] Based upon the reported rates.[13]

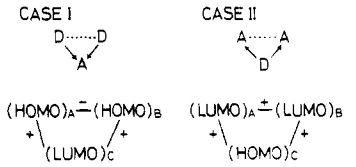

Figure 4. A conventional presentation of orbital-phase conditions for ground-state interactions.

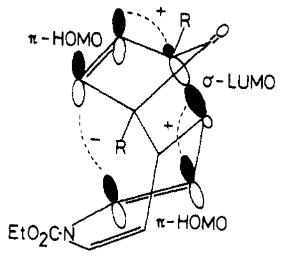

Figure 5. Three-system interactions for the Cope rearrangement.

p-cresyl ether,[14] a typical example of an ortho-Claisen-rearrangement system. This tells us that **3a–c** may rearrange by a mechanism which involves very little change in charge separation between the ground state and the transition state. On the other hand, addition to **3a** of radical chain inhibitors, such as hydroquinone, had no measurable effect on the rate. This fact suggests that the aromatic Cope rearrangement does not involve a diradical intermediate with a six-membered ring nearly dissociated into two allyl radicals.

Inagaki, Fujimoto, and Fukui[15] proposed that some organic chemical reactions can be rationalized in terms of the three-system interaction. They have drawn the orbital phase relation for an energetically favorable model of the

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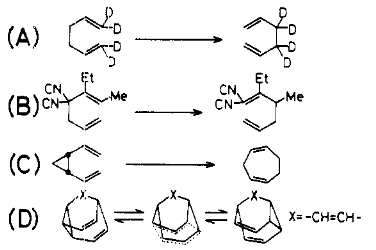
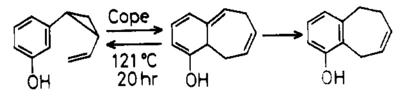


Figure 6. Typical models for the Cope rearrangements.

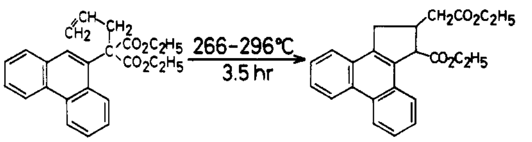
three-system interaction[16] from theoretical calculations. There are two ways of dividing three systems by their roles. They are two donors and one acceptor (case I) and two acceptors and one donor (case II) (Figure 4). In case I, the orbital phase relation for stabilization has been found[16] to be in phase (+) between the HOMO of donor A and the LUMO of acceptor C, in phase between the HOMO of donor B and the LUMO of acceptor C, and out of phase (−) between (HOMO)A and (HOMO)B, according to convention. In case II, each relation should be in phase between (LUMO)A and (HOMO)C, between (LUMO)B and (HOMO)C, and between (LUMO)A and (LUMO)B as depicted in Figure 4.[16] Two orbital-interaction schemes were required to understand the mechanism of the Cope rearrangements: one for the orbital interaction weakening the C–C$_\sigma$ bond to yield a pair of allyl fragments and the other for the interaction stabilizing the transition state.[17] According to the three-system interaction theory, our case is simply described by a single scheme of the interaction among the HOMO's of the two π bonds and the LUMO of the σ bond. Only cyclic (HOMO, LUMO, HOMO) interaction is depicted in Figure 5. The phenyl groups lower the σ-LUMO,[18] whereas the enamine group raises the π-HOMO, and thus the frontier-orbital interaction becomes quite favorable. The substituent effect of phenyl groups on the rearrangement rate has been observed. In the case of **3b**, the *p*-chlorophenyl group lowers the LUMO of the σ bond, and the HOMO–LUMO energy gaps between the π bond and the σ bond decrease, resulting in rate enhancement, whereas the reverse is true for the case of **3c** (see Table I). From this fact, the rearrangement might be interpreted in terms of the three-system interaction.

It is worthwhile to examine the application frontier MO theory to a few of the available examples. Sunko and co-workers have found that the Cope rearrangement shown in Figure 6B has an activation energy of 25.8 kcal mol^{-1}, much lower than the E_a of 33 kcal mol^{-1} measured for the Cope rearrangement of 1,1,6,6-tetradeuterio-1,5-hexadiene[19,20] in Figure 6A. This rate enhancement may be explained by the substituent effect in the three-system interaction, a favorable homodiene (HOMO)–σ-LUMO interaction. The homo-1,5-diene system shown in Figure 6C is interesting. The activation energy for the Cope rearrangment in the cyclopropyl case is about 21 kcal mol^{-1}.[21] The much lower activation energy can be attributed to the steric-release control of the cyclopropyl group in the transition state. The Cope rearrangement of bullvalene in Figure 6D has an activation energy of 11.8 kcal mol^{-1}.[22] The activation barrier to this rearrangement can be decreased still further, because the Cope rearrangement readily makes all carbon atoms equivalent. This extremely facile rearrangement in bullvalene is attributed to the partial release of strain energy through the formation of the transition state and to the proximity (2.53 Å)[23] of the nonbonded terminal of the divinylcyclopropane unit in the ground state.

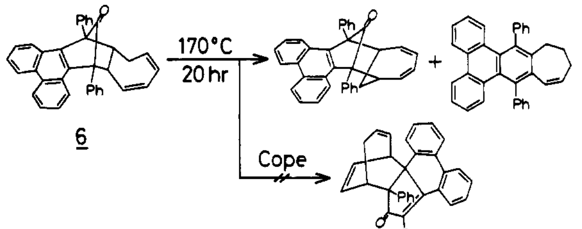
Scheme II



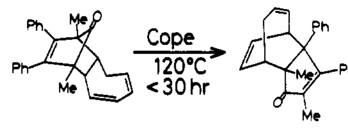
Scheme III



Scheme IV



Scheme V



On the other hand, so far as we know, there are few examples of the aromatic Cope rearrangement. Recently, Marvell and Lin[2] demonstrated the aromatic Cope rearrangement of *cis*-1-(3-hydroxyphenyl)-2-vinylcyclopropane without success in trapping the Cope rearrangement product via Diels–Alder adduct (Scheme II). Use of naphthalene or phenanthrene rings with activated molecules such as diethyl α-allyl-α-(2-naphthyl)malonate or diethyl α-allyl-α-(9-phenanthryl)malonate gave products of a complex rearrangement, which might result from further reaction of an initial Cope rearrangement product, though the mechanism is still unknown[2] (Scheme III).

In contrast to the severe reaction conditions of Marvell's study, our aromatic Cope rearrangement takes place rapidly under mild conditions at room temperature. When these facts are taken into consideration, the reason for this surprising result may be ascribable to the following: the effective orbital interactions in the three-system by activating groups; the favorable preorientation of the diallylic system imposed by the fixed geometry of the bicyclic structure. In addition to these factors, steric-release control of the bicyclo[2.2.1]heptan-7-one moiety seems to be important in this rearrangement.

It seems likely that the positive $\Delta S^{\ddagger}$ value suggests the rearrangement via a less highly ordered transition state than the ground state, e.g., a diradical mechanism. If diradicals were involved, the same rearrangement should be observed in the endo-[4 + 2]-π cycloadduct (**6**) similar

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in structure to **3a**, of phencyclone (**1a**) and cycloheptatriene.[24] Contrary to this expectation, heating cycloadduct **6** at 170 °C for 20 h caused merely 1,5-sigmatropic rearrangement and a decarbonylation reaction[24] (Scheme IV). Note that the destruction of aromaticity in **3** seems to be energetically unfavorable.

In contrast, the endo adduct of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**5**) and cycloheptatriene rearranges completely to the Cope rearrangement product at 120 °C after less than 30 h[25] (Scheme V).

In addition to the facts stated above, the diradical intermediate can be ruled out from the stereospecificity of product formation and the lack of diradical coupling products; the reactions here, as for **3a–c**, must be called "concerted" reactions assisted by substituent effects.

Thus, the positive value of $\Delta S^{\ddagger}$ for the process may be attributed to a ground state for the aromatic Cope rearrangement of the endo-[4 + 2]-π cycloadduct **3a** having more stringent geometrical constraints than the transition state. The conformation of **3a** in the ground state may be less conformationally mobile,[26] i.e., more rigid, than that in the transition state.

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. UV spectra were determined with a Hitachi EPS-3T spectrophotometer. ^{1}H NMR spectra were taken with a JEOL PS-100 spectrometer with Me_4Si as an internal standard; chemical shifts are expressed in δ values. ^{13}C NMR spectra were recorded on a JEOL FX-100 with Me_4Si as internal standard. IR spectra were taken with a JASCO DS-701G infrared spectrophotometer.

Cycloaddition Reactions of Phencyclone Derivatives 1 with *N*-(Ethoxycarbonyl)azepine (2). A solution of phencyclone (**1a**)[24] and a slight excess of **2** was allowed to stand at room temperature until the deep green color faded away. The mixture was diluted with methanol and the precipitated solid was filtered off and washed with methanol several times.

3a was obtained as colorless prisms: mp 156.5–162 °C dec; IR (Nujol) 1786 (bridged C=O), 1730 (urethane C=O), 1682 (C=CNC=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, CH_3), 3.66 (q, 2 H, CH_2), 4.16 (d, 2 H, H_c), 5.32 (dd, 2 H, H_b, $J_{ab} = 10$, $J_{bc} = 4$ Hz), 6.20 (d, 2 H, H_a), 7.0–7.80 (m, 16 H, aromatic H), 8.62 (d, 2 H, H_f); ^{13}C NMR ($CDCl_3$) 13.89 (q, CH_3), 41.13 (d, C_c), 62.46 (t, CH_2), 66.97 (s, C_d), 108.28 (d, C_a), 195.87 (s, C_e) ppm; UV λ_{max} (EtOH) 253 nm (log ϵ 4.60), 312 (3.85). Anal. ($C_{38}H_{29}NO_3$) C, H, N.

3b was obtained as colorless powder: mp 183–189.5 °C dec; IR (Nujol) 1784 (bridged C=O), 1732 (urethane C=O), 1690 (C=CNC=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 3.66 (q, 2 H), 4.14 (d, 2 H), 5.25 (dd, 2 H, $J = 10$, $J = 4$ Hz), 6.22 (d, 2 H), 6.96–7.80 (m, 14 H, aromatic H), 8.64 (d, 2 H). Anal. ($C_{38}H_{27}Cl_2NO_3$) C, H, N.

3c was obtained as colorless powder: mp 155.5–160 °C dec; IR (Nujol) 1781 (bridged C=O), 1727 (urethane C=O), 1689 (C=CNC=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 3.69 (q, 2 H), 3.88 (s, 6 H), 4.14 (d, 2 H), 5.33 (dd, 2 H, $J = 10$, $J = 4$ Hz), 6.21 (d, 2 H), 6.84–7.72 (m, 14 H, aromatic H), 8.62 (d, 2 H). Anal. ($C_{40}H_{33}NO_5$) C, H, N.

Aromatic Cope Rearrangement of Endo-[4 + 2]-π Cycloadducts 3 to Anti-Endo-[2 + 4]-π Cycloadducts 4. A solution of **3a** (0.5 g) in benzene (5 mL) was heated at 80 °C for 2 h. The solvent was evaporated under reduced pressure and the residue was recrystallized from benzene–methanol to give **4a** (0.498 g), quantitatively, as nearly colorless cubes: mp 251–252 °C; IR (Nujol) 1714, 1700 (urethane or enone C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.56 (t, 3 H), 3.48 (q, 2 H), 3.82 (dd, 1 H), 5.12 (m, 2 H), 5.46 (d, 1 H), 6.60–6.68 (m, 2 H), 6.68–7.80 (m, 18 H, aromatic H); ^{13}C NMR ($CDCl_3$) 13.83 (q), 34.63 (d), 55.05 (d), 61.53 (t), 67.50 (s), 106.56 (d), 139.16 (s), 153.05 (s), 203.91 (s); UV λ_{max} (EtOH) 255 nm (log ϵ 4.39), 323 (3.92). Anal. ($C_{38}H_{29}NO_3$) C, H, N.

From 0.5 g of **3b** was isolated 0.497 g of **4b**: mp 216.5–222 °C dec; IR (Nujol) 1728, 1712 (urethane or enone C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H), 3.50 (q, 2 H), 3.68 (dd, 1 H), 4.80–5.04 (m, 1 H), 5.36 (dd, 1 H), 5.64 (dd, 1 H), 6.52–6.66 (m, 2 H), 6.32–8.00 (m, 16 H, aromatic H). Anal. ($C_{38}H_{27}Cl_2NO_3$) C, H, N.

From 0.5 g of **3c** was isolated 0.495 g of **4c**: mp 209–210.5 °C; IR (Nujol) 1714, 1700 (urethane or enone C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 3 H), 3.54 (q, 2 H), 3.66 (s, 3 H), 3.78 (s, 3 H), 3.82 (dd, 1 H), 4.72–5.04 (m, 1 H), 5.48 (dd, 1 H), 6.52–6.68 (m, 16 H, aromatic H). Anal. ($C_{40}H_{33}NO_5$) C, H, N.

Kinetics. The rate of rearrangement of **3** was followed at a given temperature by measuring the increase of the enone absorption at 330 nm, using a 10 × 10 mm quartz cell which was thermostated with flowing water at constant temperature. The first-order rate constants (k_1) were calculated from a plot of ln $(A_t - A_\infty)/(A_0 - A_\infty)$ vs. time by a least-squares method, where A_t is the absorbance at time t and A_∞ is the absorbance after about 10 half-lives. The kinetic data are listed in Tables I and II.

X-ray Diffraction. Cubic crystals of **4a** grown from ethanol/acetone solution were obtained. X-ray intensity data were collected on a Syntex P$\bar{1}$ four-circle diffractometer with the $\theta - 2\theta$ scan mode, using a scan speed of 24 to 4°/min. Data were collected with Mo Kα radiation to a scattering angle of $2\theta \leq 55°$ for a total of 3990 reflections, from which 1927 independent reflections with $I > 2\sigma(I)$ were obtained. Lorentz and polarization corrections were applied. The space group is $P2_1/n$, a nonstandard setting of $P2_1/c$ (C_{2h}^5, No. 14), with cell parameters $a = 15.119$ (10), $b = 14.532$ (6), $c = 13.042$ (10) Å, $\beta = 91.40$ (6)°, $Z = 4$, $V = 2865$ (3) Å^3, $D_c = 1.270$, and $D_m = 1.259$ g/cm^3.

An overall temperature factor of 2.67 Å^2 was obtained from a Wilson plot and used to calculate normalized structure factors.[28] The phases of 467 reflections with $E \geq 1.5$ were developed by weighted multisolution tangent refinement (MULTAN),[29] using three defining phases (1, 11, –7; 10, 1, 6; 11, 4, –8) and 0, 4, 2; 1, 4, –10; 1, 4, –1; 10, 8, 2; 11, 1, 7 as multisolution phases. All nonhydrogen atoms were located from an E-map based on the phase set with figure-of-merit 1.247.

This model was refined to R 0.119 by a block-diagonal least-squares (isotropic vibration) technique and further to R 0.072 with anisotropic temperature factors. A difference Fourier map now revealed all hydrogen atoms. At this stage, the full set of data became available and refinement was continued with the hydrogen atoms incorporated into the model with fixed isotropic temperature factors. In all stages of refinement, each reflection was assigned a weight (w), where $w = 1.0$; refinement converged at R 0.068.

All the calculations unless stated were performed on the FACOM M-190 computer in the Computer Center of Kyushu University with the Universal Crystallographic Computation Program System UNICS II.[30]

Registry No. 1a, 5660-91-3; **1b**, 62336-65-6; **1c**, 62336-67-8; **2**, 2955-79-5; **3a**, 73333-41-2; **3b**, 73333-42-3; **3c**, 73333-43-4; **4a**, 73333-44-5; **4b**, 73347-51-0; **4c**, 73333-45-6.

Supplementary Material Available: Tables of bond lengths (Table IV), bond angles (Table V), anisotropic thermal parameters for the nonhydrogen atoms (Table VI), and coordinates for hydrogen atoms (Table VII) (4 pages). Ordering information is given on any current masthead page.

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(26) The NMR spectra of the cycloadduct from **1a** and various dienophiles always show the signals derived from solvents, e.g., benzene or methanol, incorporated by electrostatic attractions of the phenanthrene ring moiety. The X-ray analyses[1b,27] also support this observation. From these facts, the less mobile ground state may be ascribed to complex formation between the phenanthrene ring moiety and the solvent.

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