Cyclization of Electron-Deficient Cyclopentadienone with 2-Alkenyl and 2-Alkynylamines via Sequential Pericyclic Reaction Pathway

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The pericyclic reactions of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) with both allylic and propargylic amines have been investigated. The reaction proceeded via initial formation of the 1,4 adducts followed by the ene cyclization and/or sequential pericyclic reactions depending upon the structures of the amines. The reaction of **1a** with diallylamine (**2a**) gave the tetracyclic compound (**3a**). On the other hand, the reaction of **1a** with 2-propynylamine (**2c**) gave exclusively the bicyclic compound (**5c**). In the reactions with the secondary 2-propynylamines (**2d,e**), the tetracyclic compounds (**3d,e**) were exclusively formed. The reactions of **1a** with α-branched primary 1,1-dialkyl-2-propynylamines (**2f,g**) gave mixtures of **3**- and **5**-type compounds. The tetracyclic compounds **3** were formed from the intramolecular [4+2]π cycloadditions of the [1,5]-sigmatropic rearrangement products of the 1,4 adducts of **1a** and **2**, followed by the [1,5]-sigmatropic rearrangement of hydrogen and dehydrogenation. The bicyclic compounds **5** were derived from the [2π+2π+2σ] reaction of the 1,4 adducts of **1a** and **2**. The one-pot multistage sequential pericyclic reactions were discussed on the basis of the X-ray crystallographic structures and the MO calculation data.

Introduction

Cyclopentadienones (**1**) are antiaromatic diene components[1] having very low lowest unoccupied molecular orbital (LUMO) energy levels. However, there are not many cyclopentadienones existing as monomers. Of those, 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**), which exists as a monomer, is a powerful 4π source, and a systematic study of the pericyclic reactions of **1a** with various unsaturated compounds was made by Kanematsu and associates.[2] On the other hand, it is well-known that **1a** also shows high reactivity toward alcohols or amines to give the 1,4 adducts.[3] The preconception about the priority of 1,4 addition over cycloaddition seems to prevent the detailed study of the cycloaddition reaction of **1a** with unsaturated compounds bearing a hydroxy or an amino group.

During the course of a study on the pericyclic reaction behavior of cyclopentadienones, we found that **1a** reacted with allylic alcohols to give the [4+2]π cycloadduct.[4] On the other hand, in the reaction with diallylamine (**2a**), we isolated the 2a,3,4,4a,5,9c-hexahydro-3-aza-pentaleno-[1,6-*ab*]naphthalen-2-one derivative (**3a**) as a one-pot reaction product, without knowing its formation mechanism.

On the basis of these backgrounds, we considered that a marked difference in the reaction behavior between the hydroxy- and amino-substituted alkenes depends on the characters of their HOMO and the novel tetracyclic compound **3a** is presumably derived from the 1,4 adduct of **1a** and **2a**.

We now discuss the reactions in detail, with newly obtained data, to clarify the overall character of the cyclization reactions of **1a** with unsaturated amines.

Results and Discussion

Theoretical Consideration of the Reaction Behavior of Cyclopentadienones (1a) toward Diallylamines (2a). To know the reaction behavior of **1a**, the MNDO-PM3[5] calculations were carried out. The frontier molecular orbital (FMO) energy levels and coefficients of **1a** and **2a** are graphically represented in Figure 1, which involves the FMO of allyl alcohol. As can be seen in Figure 1, the interaction between the LUMO of **1a** and the HOMOs of the olefins plays a leading role in the reactions.

The HOMO of diallylamine (**2a**) is localized at the lone pair of the nitrogen atom (*n*-HOMO), and the dienophilic π-orbital is found in the NHOMO, whereas the HOMO of allyl alcohol is π-HOMO. This implies that allylic

* Corresponding author.

(1) Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7418−7423.

(2) Harano, K.; Yasuda, M.; Ban, T.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 4455−4462. Mori, M.; Hayamizu, A.; Kanematsu, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1259−1272. Jikyo, T.; Eto, M.; Harano, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3463−3470 and references therein.

(3) Eistert, B.; Thommen, A. J. *Chem. Ber.* **1971**, *104*, 3048; Arackal, T. J.; Eistert, B. *Chem. Ber.* **1973**, *106*, 3788.

(4) (a) Harano, K.; Eto, M.; Oya, T.; Nakamoto, S.; Hisano, T. *Tetrahedron Lett.* **1992**, *43*, 6473−6476. The atomic coordinates for the nonhydrogen atoms of **3a** were communicated. (b) Eto, M.; Harano, K.; Oya, T.; Hisano, T. *Chem. Pharm. Bull.* **1993**, *41*, 97−107.

(5) PM3 calculations were performed using MOPAC ver. 6.0 (QCPE No. 445) and MOPAC97. Stewart J. J. P. *QCPE Bull.*, **1990**, *10*, 86. *MOPAC97*, Fujitsu Ltd: Tokyo, Japan, 1998.

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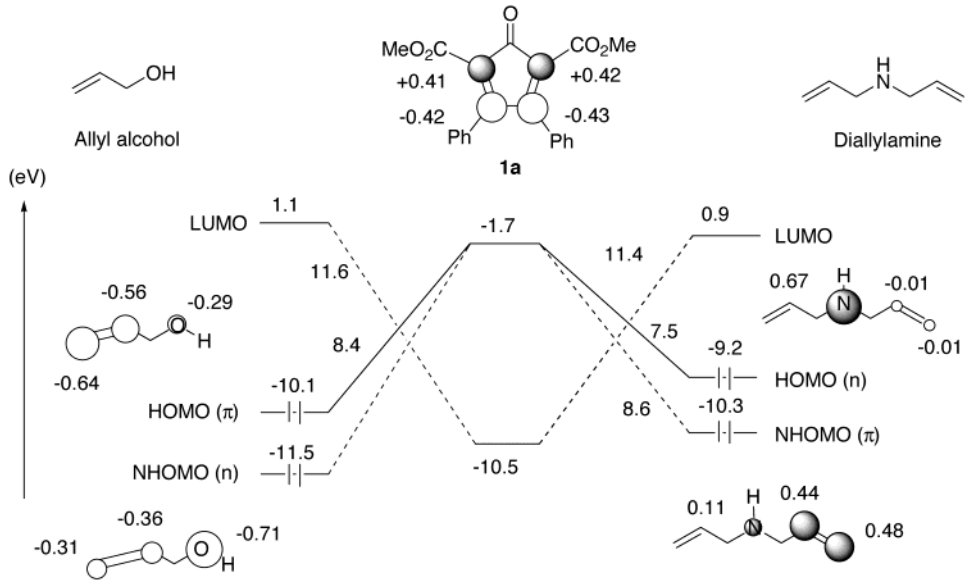


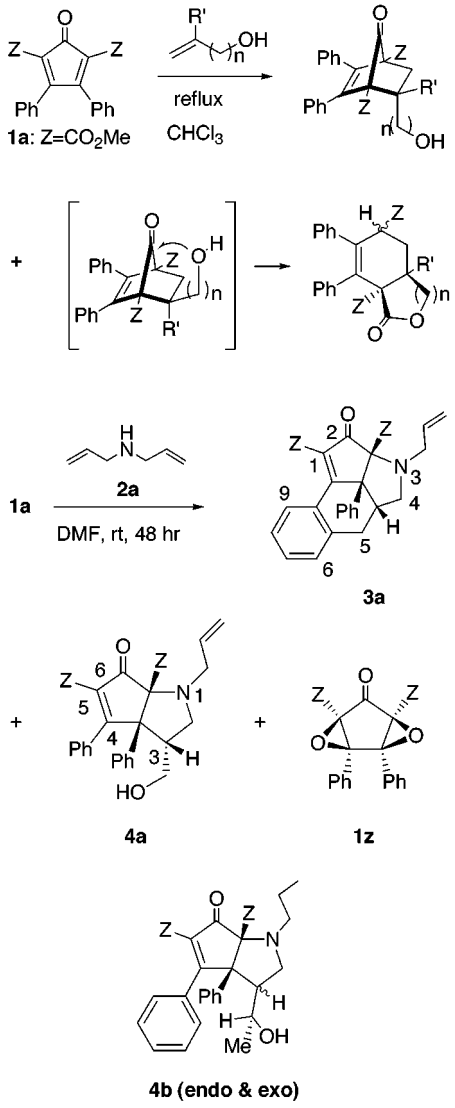
Figure 1. FMO coefficients and energy levels.

alcohols undergo [4+2]π cycloaddition and allylic amines undergo 1,4 addition.

Reaction of 1a with 2-Propenylamines (2a,b). A mixture of **1a** and **2a** in DMF was allowed to stand at room temperature until **1a** could not be recognized on the thin-layer chromatogram (TLC) of the reaction mixture. Purification of the crude product by chromatography on silica gel with *n*-hexane-benzene elution afforded three products (**3a**, **4a**, and **1z**). The mass spectrum of **3a** showed a dehydrogenated 1:1 adduct of **1a** and **2a**. The IR spectrum showed a conjugated carbonyl absorption band at 1706 cm^{-1}, and UV−vis absorption spectrum showed an n−π* absorption, indicating the presence of the 2-methoxycarbonyl-3-phenylcyclopentenone moiety. The ^1H NMR spectrum exhibited that the three olefinic hydrogens of an *N*-allyl group changed to the hydrogens on sp^3 carbons. The ^{13}C NMR spectra supported this assignment. The ^1H detected heteronuclear multiple bond connectivity (HMBC) spectrum and numbers of aromatic protons (9H) suggested that the terminal carbon of an allyl group connected with the 2-position of a phenyl group. The methyl protons of a methoxycarbonyl group showed high-field shift [δ 3.02 for C(2a)−CO_2Me] compared with the other methyl group [δ 3.89 for C(1)−CO_2Me], implying that the ester and the 9C-phenyl groups are in a nearly face-to-face disposition. To clarify the full structure of **3a**, a single-crystal X-ray analysis was performed. Compound **3a** has isoindole skeleton condensed with benzene and cyclopentenone rings, which is assumed to be formed from intramolecular cycloaddition of the aromatic diene (styrene moiety) with the allyl group (Figure S1).

Compound **4a** has molecular formula of $C_{27}H_{27}NO_6$, which corresponds to **1a** + **2a** + oxygen. The IR and UV spectra are similar to those of **3a**. The IR spectrum exhibited hydroxy and enone absorption bands. The latter was confirmed by the vis absorption spectral data. The NMR spectral data showed adjacent three sp^3 carbons. The HMBC spectrum showed correlation between 3-H and 4-C, implying the formation of a pyrrolidine ring condensed with the cyclopentenone moiety (2,3,3a,6a-tetrahydro-1*H*-cyclopenta[*b*]pyrrol-6-one skeleton). The structure was confirmed by the X-ray analysis of the

Scheme 1



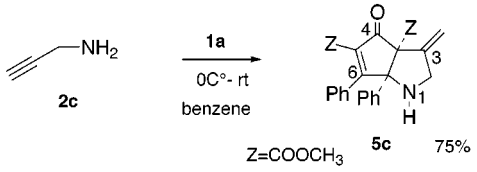
analogue (**4b**) derived from the reaction of 2-butenyl(*n*-propyl)amine (**2b**) with **1a** (Figure S2 and Scheme 1).

Table 1. Product Distribution for the Reaction of 1a with 2a[a]

			yield (%)			
solvent	temp. (°C)	time (h)	**3a**	**4a**	**1z**	total
DMF	r.t.	48	25	15	6	46
DMF (deairing)	r.t.	48	37	10	–	47
DMF (deairing)	0	72	14	30	–	44
toluene (deairing)	0	72	8	31	–	39

[a] 1:1 reaction.

Scheme 2



The structure of **1z** was determined as a diepoxide of **1a** on the basis of the MS data. The high-field shift of the phenyl protons indicates the stereochemistry of the diepoxide to be syn. The formation of **1z** is suppressed under deairing conditions (see Table 1). When a mixture of **1a** and triethylamine in toluene was stirred at room temperature, **1z** was produced. The diepoxide **1z** is considered to be derived from the [4+2]π cycloadduct of **1a** and oxygen.[6]

The product distributions under some different conditions are tabulated in Table 1. The reaction did occur even at 0°, wherein the formation of **4a** is predominant. A dipolar aprotic solvent (DMF) was found to be a suitable solvent for the reaction. In the case of toluene at 0°, the formation of a small amount of the Diels–Alder adduct was also observed. Several 2-alkenylamines were allowed to react with **1a**, but the yields were low.

Reaction of 1a with 2-Propynylamines (2c–g). A mixture of **1a** and 2-propynylamine (**2c**) in acetonitrile was allowed to stand at 0 °C or room temperature for 4h under an argon gas atmosphere. The crude product was purified by chromatography on silica gel to give **5c** (Scheme 2). Inspection of the ^{1}H NMR and ^{13}C NMR spectra of **5c** indicated the presence of the exocyclic vinyl group and the three sp^3 carbon atoms, except for the two methoxy groups. The IR and visible absorption spectra implied the presence of the phenyl-conjugated cyclopentenone structure. These suggest the formation of 3-methylenepyrrolidine ring.

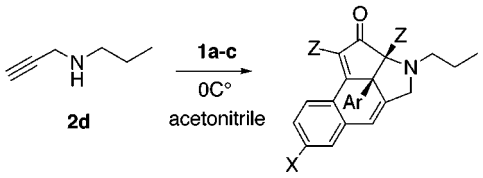
The regiochemistry of the cyclization was established by the single-crystal X-ray analysis, showing that the nitrogen atom of **2c** attached to the β position of the cyclopentadienone ring (Figure S3). The Diels–Alder reaction product was not produced, indicating that the nitrogen lone pair is more reactive than the acetylenic π orbitals, in accordance with the FMO consideration.

Propyl(2-propynyl)amine (**2d**) reacted with **1a** under the same reaction condition to give the tetracyclic compound (**3da**) (see Scheme 3).

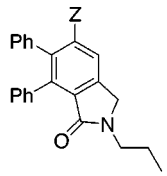
The structure was determined by comparison of the ^{1}H NMR spectrum with that of **3e** derived from the reaction of **1a** with di(2-propynyl)amine (**2e**), whose structure was confirmed by the X-ray crystallography (see Scheme 4 and Figure S4).

(6) Oxygen may be activated by light in the presence of strong electron-donating amines. The isolation of the [4+2]π cycloadduct of teracyclone and singlet oxygen was reported. Chan N. W. S. *Chem. Commun.* **1970**, 1550.

Scheme 3



X=H, Ar=phenyl	**3da**	41%
X=OMe, Ar=4-methoxyphenyl	**3db**	45%
X=Br, Ar=4-bromophenyl	**3dc**	42%



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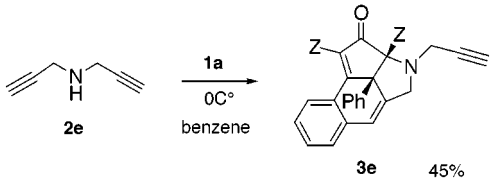
by-product

Scheme 4



The reactions of 2,5-bis(methoxycarbonyl)-3,4-di-(4-methoxyphenyl)cyclopentadienone (**1b**) and 2,5-bis-(methoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone (**1c**) with **2d** afforded the similar adducts (**3db** and **3dc**) (see Scheme 3).

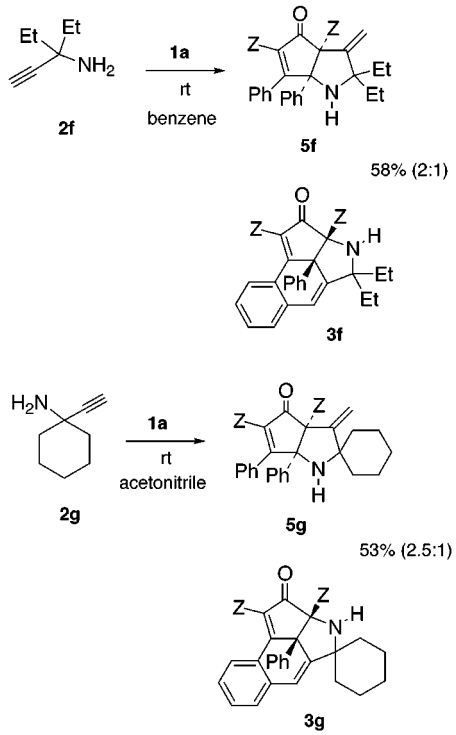
The reactions with 1,1-Diethyl-2-propynylamine (**2f**) and 1-ethynylcyclohexylamine (**2g**) gave the bicyclic compound (**5f,g**), together with the tetracyclic compounds (**3f,g**). The results are shown in Scheme 5.

As described above, the reaction with the unsubstituted primary amine (**2c**) gave the bicyclic compound, whereas the reactions with the secondary amines (**2d,g**) gave the tetracyclic compounds. The reactions with primary amines (**2f,g**) branched at the α position gave mixtures of the bicyclic and tetracyclic compounds.

In the reactions studied, a marked reactivity difference between 2-alkenylamines and 2-alkynylamines was observed. Allylamine reacted with **1a** but did not produce the bicyclic compound such as **5c** obtained in the reaction of **1a** with **2c**. The reaction product was a mixture of the 1,4 adduct and its 1,5 sigmatropic rearrangement product, which readily decomposed to the starting materials. In the formation reaction of the tetracyclic compounds **3**, the substituent effect of 2-alkenyl moiety is significant. For example, the reaction of **1a** with 2-butenylpropylamine (**2b**) gave the tetracyclic **3b** (8%) and bicyclic compounds **4b** (7%) in poor yields. The difference in reactivity between 2-alkenylamines and 2-alkynylamines is attributable to the steric repulsion between the olefinic protons of **2** and the residual moieties in the pericyclic transition-state structures, besides their intrinsic reactivity difference between alkene and alkyne observed in pericyclic reactions.[7]

(7) Ciganek, E. *Org. React.* **1984**, *32*, 59–60 and references therein.

Scheme 5



Reaction Mechanism. The bicyclic compound (**5c**) is considered to be formed from the ene reaction of the 1,4 adduct of **1a** and **2c**. The transition structure (**TS-5c**) was successfully located by ab initio (HF) and DFT (B3LYP) calculations at 6-31G* level without simplification of the reaction system.[8] The forming C···C single bond length is 2.283Å, while the two partial O···H and C···H bond lengths are 1.150 and 1.487 Å, supporting the [$2\pi+2\pi+2\sigma$] reaction in which the acetylenic and ethylenic π bonds act as 2π and the O−H bond acts as 2σ (see Figure 2).

Next, to obtain an evidence of the 1,5 sigmatropic rearrangement of the 1,4 adduct, a model reaction was studied using aniline. When **1a** and aniline were dissolved in $CDCl_3$ at room temperature, monitoring of the ensuing reaction by analyzing the ^{1}H NMR signals of the OMe groups of **1a** at δ 3.73, **6** at δ 3.62 and 3.82, and **7** at δ 3.38 and 3.90 revealed the initial formation of **6**. As illustrated by Figure 3, the concentration of **6** increased rapidly until a maximum was reached (<10 min) and then decreased gradually with increase of **7**. From the consumption of **6** and the behavior of the other compositions (**1a** and **7**, Scheme 6), it is obvious that **6** is converted to **7**, whose structure was confirmed by the single-crystal X-ray analysis.[9]

In this reaction, a small amount of the 1,4 adduct (**6**) was isolated from the reaction of **1a** with aniline in CH_3-CN at 0 °C. The 1,4 adduct was found to be thermally stable. The 1,5 sigmatropic rearrangement did not occur by only heating at 60 °C, but in the presence of aniline, the rearrangement easily occurred. This indicates that the base-catalyzed enolization of the carbonyl group of the cyclopentenone moiety is required for the creation of the 1,5 sigmatropic rearrangement reaction system (**6′**).

From the facts described above, the tetracyclic compound is considered to be formed via the 1,5 sigmatropic

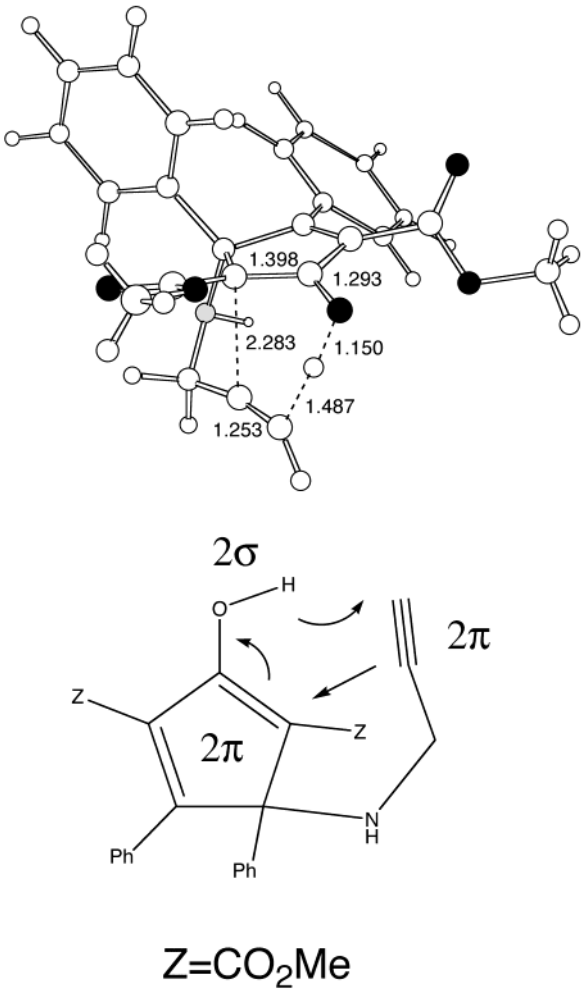


Figure 2. B3LYP/6-31G* transition structure (**TS-5c**) of the intramolecular ene reaction of the 1,4 adduct of **1a** and **2c**.

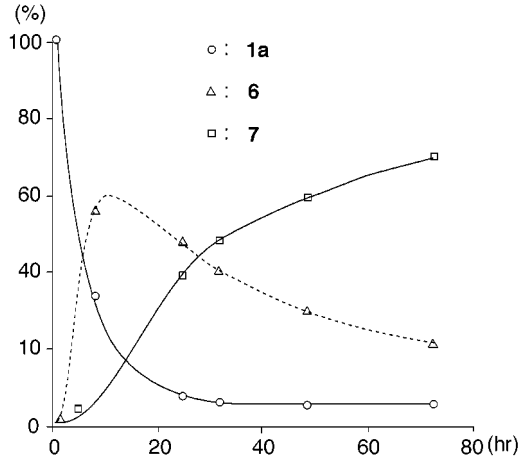
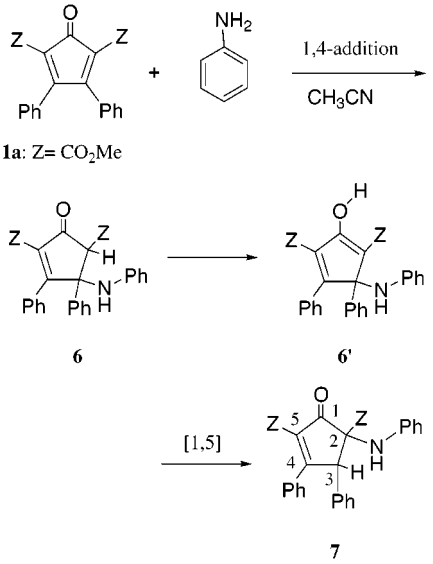


Figure 3. Time course experiment for the reaction of **1a** with aniline.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(9) Taken from: Kai, C. Master's Thesis, Kumamoto University, Kumamoto, Japan, 2000. The X-ray coordinates will be published elsewhere: Yoshitake, Y.; Kai, C.; Jikyo, T.; Harano, K. Manuscript in preparation.

Scheme 6



rearrangement product (**B**) of the 1,4 adduct (**A**) of **1a** and the unsaturated amines, followed by the intramolecular Diels−Alder (IMDA) reaction using the styrene moiety as diene and dehydrogenation of the IMDA adduct (see Scheme 7).

There are two IMDA reaction pathways (I and II) arisen from the two styrene moieties (see Scheme 8). The AM1 or PM3 transition-state calculation rules out route I because of the higher reaction barrier than that of route II because of ring strain (see Table 2).

Styrenes are usually poor dienes in the IMDA reaction because the initial step requires loss of aromatic resonance stabilization. It is noteworthy that the IMDA reactions proceed under very mild reaction conditions,[10] although the dienophile moiety is not activated at all. The DFT TS calculations (B3LYP/6-31G*) using a simplified model reaction system (**GSc** → **TSc**) suggest that the IMDA reaction has a stepwise cycloaddition character (see the forming C−C bond lengths in Figure 4 and the energetics in Table 3). The UHF/AM1 or UHF/PM3 TS calculation using the full structure also suggests the stepwise character (Figure S5).

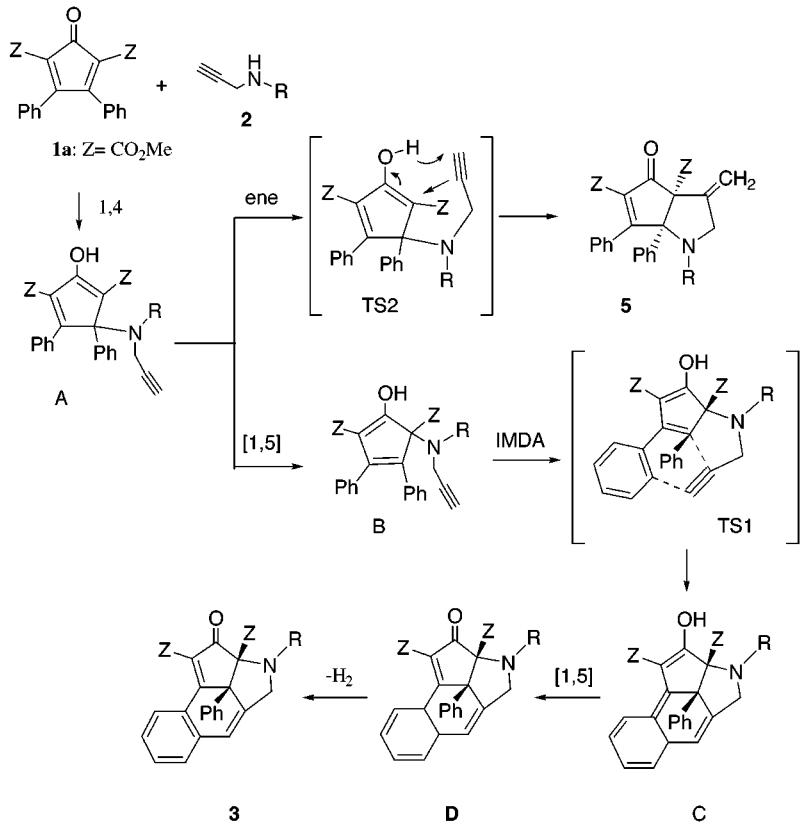
The IMDA reaction product (**C**) may transform to the dihydro derivative (**D**) by the 1,5 sigmatropic rearrangement of hydrogen (see Scheme 7).

The final stage of dehydrogenation mechanism is uncertain. In the reaction of **1a** with propyl(2-propynyl)-amine (**2d**) in toluene or with allyl *tert*-butylamine in $CHCl_3$, we isolated the [3,3]-sigmatropic rearrangement product (**8**) of the DA adduct of **1a** and the dihydropentadienone (**1a** + 2H; Scheme 9). This seems to suggest that **1a** acts as a hydrogen acceptor. However, the concentration change of **1a** did not affect the yield of **3**. At the present time, the dehydrogenation mechanism remains to be confirmed.

The FMO consideration for the reaction behavior of allylic amines toward cyclopentadienones can be applied to 2-alkyn-1-ols. Usually, 2-propyn-1-ol reacted with **1a** to give the DA adduct (**9**). However, in the presence of amines, the bicyclic compound (**10**) was produced (Scheme 10). This may be attributed to the stabilization of the alcoholate anion ($HC{\equiv}C{-}CH_2O^-$) in aprotic solvents and the acceleration of the 1,5 sigmatropic rearrangement reaction by enolization of the cyclopentenone moiety of the 1,4 adduct.

Mention should be made of a charge-transfer complex formation. At an early stage of the reaction with primary

Scheme 7



Scheme 8

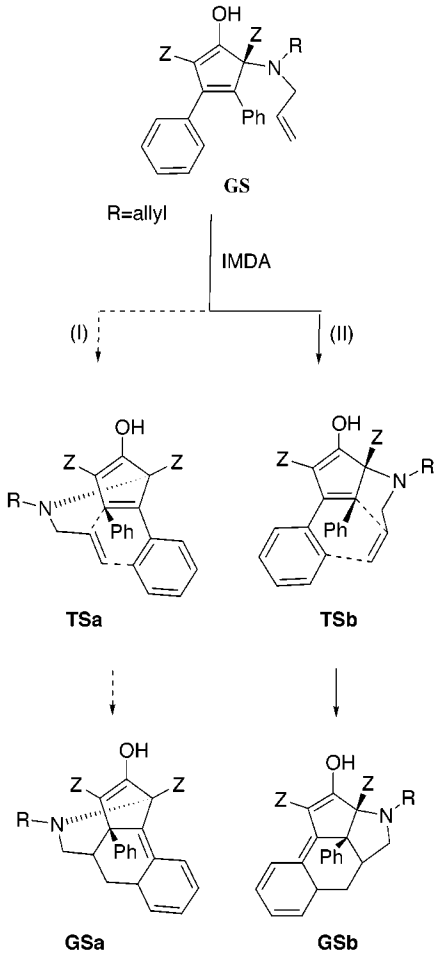


Table 2. Energetics of the Ground-State and Transition-State Structures for the IMDA Reaction Step in the Reaction of 1a with 2a (GS → TSa,b → GSa,b)

geometry	method	ΔH_f[a])	$\Delta\Delta H_f$[a]
GS	AM1	−55.66	−
	PM3	−69.84	−
TSa	AM	3.03	58.69 (**GS → TSa**)
	PM3	−16.37	53.47 (**GS → TSa**)
TSb	AM1	−10.00	45.66 (**GS → TSb**)
	PM3	−24.59	45.25 (**GS → TSb**)
GSa	AM	−42.30	13.06 (**GS → GSa**)
	PM3	−62.53	8.22 (**GS → GSa**)
GSb	AM1	−72.09	−16.43 (**GS → GSb**)
	PM3	−85.44	−15.60 (**GS → GSb**)

[a] In kcal/mol.

and secondary amines, perceptible transient color changes (orange → green) were observed. The tertiary amines such as triethylamine did not produce similar transient color changes with **1a**. These facts indicate that the hydrogen bonding to the carbonyl functions of **1a** lowers the LUMO energy level and enhances the electron acceptability, very favorable for charge-transfer complexation. 2,5-Dimethyl, 2,5-diethyl and 2,5-diphenylcyclopentadienones and phencyclone (1,3-diphenylcyclopenta-[*l*]phenanthren-2-one) did not show color changes due to

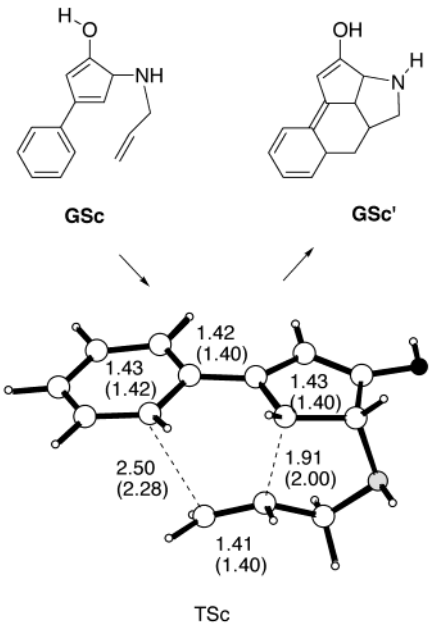


Figure 4. B3LYP/6-31G* transition structure for the model IMDA reaction (**GSc → TSc → GSc'**). HF/6-31G* bond lengths (Å) are in parenthses.

Table 3. Energetics of the Ground-state and Transition-state Structures for the Model IMDA Reaction (GSc → TSc → GSc′)

geometry	method	E[a]	ΔE[b]
GSc	RHF/3-21G	−664.3993	
	RHF/6-31G*	−668.1198	
	B3LYP/6-31G*	−672.4115	
TSc	RHF/3-21G	−664.3270	45.37 (**GSc → TSc**)
	RHF/6-31G*	−668.0322	54.97 (**GSc → TSc**)
	B3LYP/6-31G*	−672.3640	29.81 (**GSc → TSc**)
GSc'	B3LYP/6-31G*	−672.4279	−10.29 (**GSc → GSc′**)

[a] In Hartree. [b] In kcal/mol.

charge-transfer complexation but show Diels−Alder reactivity. It appears likely that 1,4 addition reaction proceeds via charge-transfer complexes.

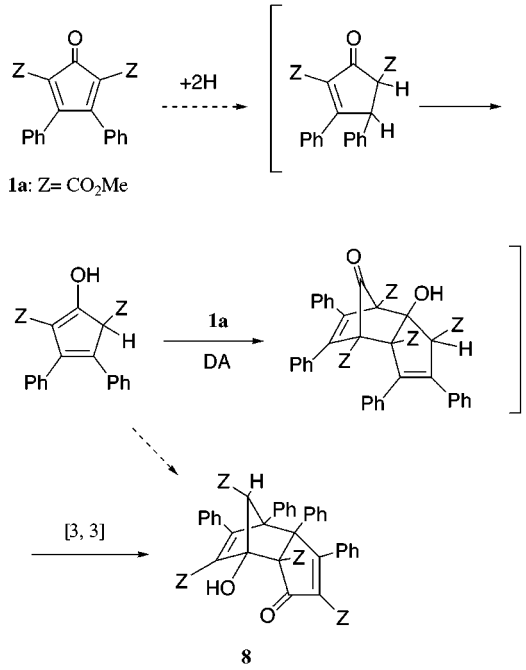
On the basis of the experimental facts, calculated TS structures, and reaction mechanism, it is reasonable to expect that the product in the reaction of **1a** with 2-alkynylamines would depend on the stability of the 1,4 adducts of **1a** and 2-alkynylamines. The addition of the secondary amines to the 3-position of **1a** produces the overcrowded 3-(primary or secondary 2-alkynylamino)-3,4-diphenylcyclopentenone derivatives. Therefore, for the relief of the strain, the 1,4 adducts may isomerize to the corresponding 1,5 sigmatropic rearrangement products leading to the tetracyclic compounds. In the case of the α-branched primary amines, the steric repulsions in the 1,4 adducts are somewhat smaller than those of the secondary amines to give the tetracyclic compounds in addition to the bicyclic compounds.

In conclusion, we have demonstrated that unsaturated amines react readily with **1a** to give bicyclic and/or tetracyclic compounds in good yield. The striking difference in the reaction behavior between allylic alcohols and allylic amines can be attributable to the character of their HOMOs. The molecular design using multistage sequential pericyclic reaction methodology is very valuable for construction of complexed molecules under very mild reaction conditions. Further generalizations of these observations and their implications for the synthesis of

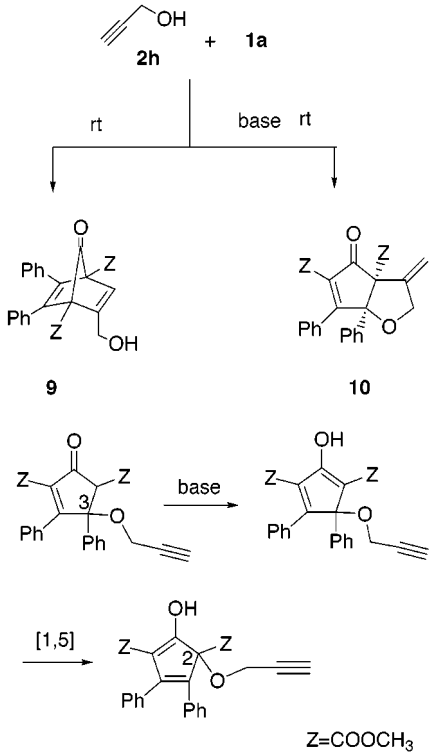
(10) Campos, P. J.; Lamaza, I.; Rodriguez, M. A.; Canal, G. *Tetrahedron Lett.* **1997**, *38*, 6741−6744. Aromatic methyleneamines (4π) react with cyclopentadiene (2π) at 40 °C to give [4+2]π adducts. The observed regio- and stereochemistry suggests a concerted mechanism for the reaction.

(11) White, D. M. *J. Org. Chem.* **1974**, *39*, 1951.

Scheme 9



Scheme 10



various heterocyclic compounds are the object of ongoing investigations.

Experimental Section

Melting points were uncorrected. The IR spectra were taken with a Hitachi 270-30 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were taken with JEOL JNM-EX 270 (270 MHz), JNM-AL 300 (300 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 spectra were recorded on a Shimadzu UV-2500PC spectrophotometer.

Materials. 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone[11] **1a** was prepared according to the previously reported method. 2,5-Bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone (**1b**) was prepared by essentially the same procedure as that described for **1a** using CH_3CN as solvent. 2,5-Bis(methoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone (**1c**) was prepared using DMF as solvent.

1b: Red prisms. mp 126−127 °C (from Et_2O). Yield 22%. IR (KBr) (cm^{-1}): 1710 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.76 (6H, s, $COOCH_3$), 3.82 (6H, s, OMe), 6.80 (4H, d, J = 9 Hz, Ar−H), 7.00 (4H, d, J = 9 Hz, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ -(ppm): 52.0 ($COOCH_3$), 55.2 (OMe), 113.1, 131.3 (Ar−C), 118.5, 123.1, 161.4, 162.1 (quaternary C), 163.0 (−COO), 190.9 (C=O). m/z (EI) 409 (M^+ + 1). Anal. Calcd for $C_{23}H_{20}O_7$: C, 67.64; H, 4.94. Found: C, 67.40; H, 4.78.

1c: Orange prisms. mp 234−235 °C (from acetone). Yield 40%. IR (KBr) (cm^{-1}): 1718 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.75 (6H, s, $COOCH_3$), 6.91 (4H, d, J = 9 Hz, Ar−H), 7.45 (4H, d, J = 8 Hz, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.3 ($COOCH_3$), 130.5, 131.3 (Ar−C), 119.6, 125.3, 129.3, 161.2 (quaternary C), 162.1 (−COO), 190.1 (C=O). m/z (EI) 506 (M^+). Anal. Calcd for $C_{21}H_{14}Br_2O_5$: C, 49.83; H, 2.79. Found: C, 50.03; H, 2.90

Cycloadditions of 1a with Unsaturated Amines (General Procedure). A mixture of **1a** (3.0 mmol) and diallylamine (**2a**) (15.0 mmol) in DMF (1 mL) was stirred at room temperature. After 72 h, the reaction mixture was diluted with benzene. The solution was 3 times washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography on silica gel with AcOEt-benzene.

With **2b**−**h**, the following products were obtained by essentially the same procedure as that described above.

Products from the Reaction of 1a with Diallylamine (2a). 3-Allyl-2-oxo-9c-phenyl-2,3,4,4a,5,9c-hexahydro-(2aa,-4aa,9ca)-3-aza-pentaleno[1,6-*ab*]naphthalene-1,2a-dicarboxylic Acid Dimethyl Ester (3a). Yellow prisms (37%). mp 130−131 °C (EtOH). IR (KBr)/cm^{-1}: 1740 (enone C=O), 1706 (ester C=O). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 2.60 (1H, t, J = 9 Hz, 4-Hβ), 2.94 (1H, d, J = 18 Hz, 5-Hβ), 3.00−2.98 (2H, m, N−CH_2 and 5-Ha), 3.02 (3H, s, −OMe), 3.47 (1H, dd, J = 9, 6 Hz, 4-Ha), 3.46−3.41 (1H, m, 4a−H), 3. 59 (1H, dd, J = 6, 14 Hz, N−CH_2), 3.89 (3H, s, −OMe), 5.09 (1H, d, J = 10 Hz, −CH=CH_2), 5.19 (1H, d, J = 17 Hz, −CH=CH_2), 5.93−5.87 (1H, m, −CH=CH$_2$), 7.30−7.05 (8H, m, Ar−H) and 7.70 (1H, d, J = 8 Hz, 9-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 194.8, 169.9, 168.9 (C=O), 164.5 (>C9b), 136.9 (C1), 135.5 (-CH=CH$_2$), 117.4 (−CH=CH$_2$), 82.8 (C2a−N), 64.7 (C9c−Ph), 53.6, 52.3, 26.3 (−CH$_2$−), 51.7, 52.6, (−OCH$_3$), 38.8 (C4a). m/z (EI) 443 (M^+). Anal. Calcd for $C_{27}H_{25}NO_5$: C, 73.12; H, 5.68; N, 3.16. Found: C, 73.32; H, 5.61; N, 3.33. The stereo structure was established by the X-ray analysis.

1-Allyl-3-hydroxymethyl-6-oxo-3a,4-diphenyl-2,3,3a,6-tetrahydro-(3aa,6aa)-1*H*-cyclopenta[*b*]pyrrol-5,6a-dicarboxylic Acid Dimethyl Ester (4a-*endo*). Yellow oil. IR (KBr)/cm^{-1}: 1724 (enone C=O), 1740 (ester C=O), 3496 (−OH). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 2.49−2.52 (1H, m, 3-Hb), 3.09, 3.82 (6H, s,-OMe × 2), 2.92 (1H, dd, J = 10, 6 Hz, 2-Hb), 3.36 (1H, d, J = 10 Hz, 2-Hα), 3.66 (1H, dd, J = 14, 6 Hz, N−CH_2−CH=), 3.03 (1H, dd, J = 8, 14 Hz, N−CH_2−CH=), 3.85 (1H, dd, J = 11, 4 Hz, −CH_2−O), 4.14 (1H, dd, J = 11, 4 Hz, −CH_2−O), 5.14 (1H, d, J = 10 Hz, −CH=CH_2), 5.24 (1H, d, J = 17 Hz, −CH=CH_2), 5.58 (1H, dddd, J = 17, 10, 8, 6 Hz, −CH=CH$_2$) and 7.27−7.52 (10H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 194.8 (C6), 176.3 (C4), 169.2 (C6a−COO−), 164.3 (C5−COO−), 135.2 (−CH=CH$_2$), 117.9 (−CH=CH$_2$), 83.8 (C6a), 70.6 (C3a-Ph), 63.0 (CH$_2$−O), 54.0 (C2), 52.2 (N−CH$_2$−CH=), 52.6, 52.1 (−OCH$_3$), 45.7(C3). m/z (EI) 461 (M^+). HRMS Calcd for $C_{27}H_{27}NO_6$ (M^+): 461.1826. Found: 461.1838.

5-Oxo-1,2-diphenyl-3,7-dioxa-tricyclo[4.1.0.0^{0,4}]heptane-4,6-dicarboxylic Acid Dimethyl Ester (1z). Colorless powder. mp 94−95 °C. IR (KBr)/cm^{-1} : 1768 (enone C=O), 1774 (ester C=O). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 3.65 (6H, s, −OMe × 2), 7.50−7.27 (10H, m, Ar−H). ^{13}C NMR (125 MHz

$CDCl_3$): 188.1(C═O), 141.0(COO), 53.1(OMe), 61.3(*C*-Ph), 76.7-(*C*−COOMe). *m/z* (EI) 380 (M^+). HRMS Calcd for $C_{21}H_{16}NO_7$ (M^+): 380.0872. Found: 380.0896.

Products from the Reaction of 1a with 2-Butenylpropylamine (2b). According to the general method, the reaction was performed in chloroform at 0 °C to give the tetracyclic (8%) and bicyclic compounds (7%).

5-Methyl-2-oxo-9c-phenyl-3-propyl-2,3,4,4a,5,9c-hexahydro-3-aza-pentaleno[1,6-*ab*]naphthalene-1,2a-dicarboxylic Acid Dimethyl Ester (3b). Yellow oil. IR (KBr)/cm^{-1}: 1705 (enone C═O), 1740 (ester C═O). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 0.89 (3H, t, J = 7 Hz, −CH_2−CH_2−CH_3), 1.42 (3H, d, J = 7 Hz, 5-Me), 1.59−1.52 (2H, m, −CH_2−CH_2−CH_3), 2.56 (1H, dd, J = 11, 9 Hz, 4b−H), 2.41−2.36 (1H, m, N−CH_2), 2.75−2.69 (1H, m, N−CH_2), 3.03 (3H, s, −OCH_3), 3.13−3.10 (1H, m, 5a−H), 3.41 (1H, dd, J = 6, 11 Hz, 4a−H), 3.50−3.47 (1H, m, 4a−H), 3.92 (3H, s, −OCH_3), 7.37−7.18 (8H, m, Ar−H) and 7.76 (1H, d, J = 7 Hz, 9-H). ^{13}C NMR (125 MHz $CDCl_3$) δ (ppm): 194.2 (>C═O), 170.1 (C2a−*C*OO), 167.9 (C9b), 164.8 (C1−*C*OO), 83.8 (C2a), 65.0 (C9c), 51.8 (C4), 50.6 (N−CH_2), 21.9 (CH_2), 45.0 (C4a), 30.2 (C5),19.2 (C5−CH_3), 11.6 (CH_3). *m/z* (EI) 459 (M^+). HRMS Calcd for $C_{28}H_{29}NO_5$ (M^+): 459.2046. Found: 459.2039.

3-(1-Hydroxyethyl)-6-oxo-3a,4-diphenyl-1-propyl-2,3,-3a,6-tetrahydro-1*H*-cyclopenta[*b*]pyrrole-5,6a-dicarboxylic Acid Dimethyl Ester (4b-*endo*). Yellow prisms. mp 174−176 °C (EtOH). IR (KBr)/cm^{-1}: 1702 (enone C═O), 1734 (ester C═O), 3572 (−OH). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 0.87 (3H, t, J = 7 Hz, −CH_2−CH_2−CH_3), 1.07 (3H, d, J = 6 Hz, −Me), 1.56−1.49 (2H, m, −CH_2−CH_2−CH_3), 2.18 (1H, d, J = 6 Hz, 3-H), 2.57 (1H, dd, J = 6, 9.8 Hz, 2-H), 2.81−2.76, 2.28 (1H, dt, J = 13, 7 Hz, −CH_2−CH_2CH_3), 3.47 (1H, d, J = 10 Hz, 2-H), 3.74, 3.04 (6H, s, −OMe × 2), 4.42 (1H, q, J = 6 Hz, >CH−OH), 7.72−7.10 (10H, m, Ar−H). ^{13}C NMR (125 MHz $CDCl_3$) δ (ppm): 194.6 (>C═O), 175.7 (C4), 169.7 (C6a−*C*OO), 164.3 (C5−*C*OO), 84.2 (C6a), 51.1 (N−CH_2−CH_2−), 48.8 (C2), 52.5, 52.1 (OCH_3), 64.6 (>CHOH), 49.1 (C1). *m/z* (EI) 477 (M^+). Anal. Calcd for $C_{28}H_{31}NO_6$: C, 70.42; H, 6.54; N, 2.93. Found: C, 70.39; H, 6.40; N, 3.05. The stereo structure was established by the X-ray analysis.

3-(1-Hydroxyethyl)-6-oxo-3a,4-diphenyl-1-propyl-2,3,-3a,6-tetrahydro-1*H*-cyclopenta[*b*]pyrrole-5,6a-dicarboxylic Acid Dimethyl Ester (4b-*exo*). Yellow oil. IR (KBr)/cm^{-1}: 1710 (enone C═O), 1744 (ester C═O), 3032 (−OH). ^{1}H NMR (500 MHz; $CDCl_3$) δ (ppm): 0.92 (3H, t, J = 7 Hz, −CH_2−CH_2−CH_3), 1.16 (3H, d, J = 6 Hz, −Me), 1.54−1.49 (2H, m, −CH_2−CH_2−CH_3), 2.67−2.64 (1H, m, 3-H), 2.74−2.68 (1H, m, N−CH_2), 3.00−2.93 (1H, m, N−CH_2), 3.16 (1H, dd, J = 7, 10 Hz, 2-H), 3.29 (1H, dd, J = 7, 10 Hz, 2-H), 3.02 (3H, s, −OMe), 3.75 (3H, s, −OMe), 4.36−4.33 (1H, m, >C*H* (OH)) and 7.60−7.26 (10H, m, Ar−H). ^{13}C NMR (125 MHz $CDCl_3$) δ (ppm): 195.8 (>C═O), 176.6 (C4), 169.0 (C6a−*C*OO), 164.4 (C5−*C*OO), 70.4 (C3a), 56.4 (C2), 50.6(N-*C*H_2−CH_2−), 52.4, 51.5 (OCH_3), 67.3 (>CHOH), 54.5 (C1). *m/z* (EI) 477 (M^+).

Products from the Reaction of 1a with 2-Propynylamine (2c). 3-Methylene-4-oxo-6,6a-diphenyl-2,3,4,6a-tetrahydro-(3aa,6aa)-1*H*-cyclopenta[*b*]pyrrole-3a,5-dicarboxylic Acid Dimethyl Ester (5c). Yellow prisms. mp 129−130 °C. IR (KBr) cm^{-1}: 1618, 1738 (C═O, COO). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.14 (3H, s, C3a-COO*C*H_3), 3.78 (3H, s, C5−COO*C*H_3), 3.62 (1H, d, J = 14.7 Hz, 2-H), 3.92 (1H, d, J = 14.7 Hz, 2-H), 5.29 (1H, s, ═CH), 5.38 (1H, s, ═CH), 7.11−7.53 (10H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 51.9 (C5−COO*C*H_3), 52.5 (C3a−COO*C*H_3), 50.3 (C2), 74.2 (C6a), 112.0 (═CH_2), 126.7, 127.7, 128.5, 128.6, 130.9 (Ar−C), 131.2, 134.5, 137.2 (quaternary C), 145.4 (C3), 163.8 (C5−*C*OO), 168.2 (C3a−*C*OO), 172.5 (C6), 192.9 (C═O). *m/z* (FAB) 404 (M^+ +1). Anal. Calcd. for $C_{24}H_{21}NO_5$: C, 71.45; H, 5.25; N, 3.47. Found: C, 71.63; H, 5.21; N, 3.17.

Reactions of 1a,b,c with Propyl(2-propynyl)amine (2d). 2-Oxo-9c-phenyl-3-propyl-2,3,4,9c-tetrahydro-(2aa, 9ca)-3-aza-pentaleno[1,6-*ab*]naphthalene-1,2a-dicarboxylic Acid Dimethyl Ester (3da). Yellow needles. mp 158−159 °C. IR (KBr) cm^{-1}: 1726 (C═O, COO). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.86 (3H, t, J = 7 Hz, N−CH_2−CH_2−CH_3), 1.45−1.52 (2H, m, N−CH_2−CH_2−CH_3), 2.86−2.95 (1H, m, N−CH_2−CH_2−CH_3), 3.00−3.10 (1H, m, N−CH_2−CH_2−CH_3), 3.04 (3H, s, C2a-COO*C*H_3), 3.86 (3H, s, C1−COO*C*H_3), 3.97 (1H, d, J = 11 Hz, 4-H), 4.22 (1H, d, J = 9 Hz, 4-H), 6.44 (1H, s, 5-H), 7.01−7.28 (8H, m, Ar−H), 7.80 (1H, d, J = 8 Hz, 9-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 11.5 (N−CH_2−CH_2−*C*H_3), 22.3 (N−CH_2−*C*H_2−CH_3), 51.1 (COOMe × 2), 52.3 (N−*C*H_2−CH_2−CH_3), 58.6 (C4), 65.7 (C9c), 79.8 (C2a), 120.2 (C5), 127.2, 127.3, 127.4, 127.8, 128.3, 128.9, 129.0, 131.9 (Ar−H), 127.6, 128.1, 134.0, 137.2 (quaternary C), 162.9 (C1−*C*OO), 168.9 (C2a−*C*OO), 177.7 (C9b), 196.9 (C═O). *m/z* (EI) 443 (M^+). Anal. Calcd. for $C_{27}H_{25}NO_5$: C, 73.12; H, 5.68; N, 3.16. Found: C, 73.18; H, 5.66; N, 3.24.

In the reaction of **1a** with **2d** in toluene, small amounts of the byproducts (**8**, **11**) were isolated. The product **11** is the aromatized compound of the Diels−Alder adduct of **1a** and **2d**.

4-Hydroxy-3-oxo-1,6,7,7a-tetraphenyl-3,4,7,7a-tetrahydro-4,7-methano-indene-2,3a,5,8-tetracarboxylic Acid Tetramethyl Ester (8). Colorless powder. mp 256−259 °C. IR (KBr) (cm^{-1}): 3280 (−OH), 1742 (−COO), 1705 (C═O). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.23, 3.52, 3.61, 3.93 (12H, s, $COOCH_3$ × 4), 4.56 (1H, s, methine), 7.00−8.00 (20H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 62.1 (>CH−), 73.1 (>C(Ph)−), 77.4 (>C($COOCH_3$)−), 97.2 (C−OH), 162.6, 168.7, 169.8, 172.5 (−COO), 188.1 (C═O). *m/z* (EI) 698 (M^+). This type of compound was also isolated in the reaction of **1a** with allyl *tert*-butylamine.

1-Oxo-6,7-diphenyl-2-propyl-2,3-dihydro-1*H*-isoindole-5-carboxylic Acid Methyl Ester (11). Orange oil. IR (KBr) (cm^{-1}): 1702 (C═O), 1738 (−COO). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.92 (3H, t, J = 7 Hz, N−CH_2−CH_2−CH_3), 1.66 (2H, q, J = 7 Hz, N−CH_2−CH_2−CH_3), 3.49−3.52 (2H, m, N−CH_2−CH_2−CH_3), 3.52 (3H, s, $COOCH_3$), 4.43 (2H, s, methylene), 6.96−7.40 (10H, m, Ar−H), 7.81 (1H, s, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 11.3 (N−CH_2−CH_2−*C*H_3), 21.5 (N−CH_2−*C*H_2−CH_3), 44.1 (N−*C*H_2−CH_2−CH_3), 48.7 (methylene), 52.1 (COO*C*H_3), 122.2, 126.7, 126.9, 127.2, 127.9, 128.1, 128.2, 128.6, 128.7, 129.8, 130.1 (Ar−C), 127.8, 132.0, 135.2, 138.3, 140.4, 140.6, 141.3 (quaternary C), 166.8 (−COO), 168.9 (C═O). *m/z* (EI) 385 (M^+). HRMS Calcd for $C_{25}H_{23}NO_3$ (M^+): 385.16778. Found: 385.16865.

4-Methoxyphenyl Derivative (3db). Yellow needles. mp 150−151 °C (from EtOH). IR (KBr) (cm^{-1}): 1712 (C═O), 1732 (−COO);^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.86 (3H, t, J = 7 Hz, N−CH_2−CH_2−CH_3), 1.46−1.50 (2H, m, N−CH_2−CH_2−CH_3), 2.89−2.95 (1H, m, N−CH_2−CH_2−CH_3), 3.02−3.05 (1H, m, N−CH_2−CH_2−CH_3), 3.10 (3H, s, $COOCH_3$), 3.68, 3.74 (6H, s ×2, OMe ×2), 3.85 (3H, s, $COOCH_3$), 3.95 (1H, d, J = 11 Hz, 4-H), 4.21 (1H, d, J = 11 Hz, 4-H), 6.37 (1H, s, 5-H), 6.56−6.66 (6H, m, Ar−H), 7.84 (1H, d, J = 9 Hz, 9-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 11.6 (N−CH_2−CH_2-*C*H_3), 22.4 (N−CH_2-*C*H_2 CH3), 51.2, 52.3 (COO*C*H_3 ×2), 52.4 (N-*C*H_2−CH_2−CH_3), 55.1, 55.3 (OMe ×2), 58.6 (C4), 65.6 (C9c), 79.7 (C2a), 111.8, 113.7 (Ar−C), 120.0 (C5), 131.1 (C9), 121.4, 126.3, 129.6, 136.2, 147.8, 159.0, 162.6 (quaternary C), 163.2 (C1-*C*OO), 169.2 (C2a-*C*OO), 178.6 (C9b), 196.7 (C═O). *m/z* (EI) 503 (M^+). Anal. Calcd for $C_{29}H_{29}NO_7$: C, 69.17; H, 5.80; N, 2.78. Found: C, 69.07; H, 5.80; N, 2.82.

4-Bromophenyl Derivative (3dc). Yellow needles. mp 185−187 °C (from EtOH). IR (KBr) (cm^{-1}): 1718 (C═O), 1734 (−COO). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.85 (3H, t, J = 7 Hz, N−CH_2−CH_2−CH_3), 1.44−1.54 (2H, m, N−CH_2−CH_2−CH_3), 2.87−2.94 (1H, m, N−CH_2−CH_2−CH_3), 3.00−3.09 (1H, m, N−CH_2−CH_2−CH_3), 3.13, 3.85 (6H, s × 2, $COOCH_3$ × 2), 3.97 (1H, d, J = 11 Hz, 4-H), 4.19 (1H, d, J = 11 Hz, 4-H), 6.39 (1H, s, 5-H), 7.09−7.47 (6H, m, Ar−H), 7.71 (1H, d, J = 8 Hz, 9-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 11.5 (N−CH_2−CH_2−*C*H_3), 22.2 (N−CH_2−*C*H_2−CH_3), 51.4, 52.5 (COO*C*H_3 × 2), 52.3 (N-*C*H_2−CH_2−CH_3), 58.4 (C4), 65.0 (C9c), 79.4 (C2a), 119.5 (C5), 128.3, 130.3, 130.5, 130.6 (Ar−C), 122.3, 126.6, 127.0, 128.0, 135.6, 135.9, 147.5 (quaternary C), 162.5 (C1−*C*OO), 168.6 (C2a-*C*OO), 175.6 (C9b), 195.8 (C═O). *m/z* (EI) 602 (M^+ + 1). Anal. Calcd for $C_{27}H_{23}Br_2NO_5$: C, 53.93; H, 3.86; N, 2.33. Found: C, 54.16; H, 4.14; N, 2.31.

Products from the Reaction of 1a with Di(2-propynyl)-amine (2e). 2-Oxo-9c-phenyl-3-prop-2-ynyl-2,3,4,9c-tetrahydro-(2aa,9ca)-3-aza-pentaleno[1,6-*ab*]naphthalene-1,2a-dicarboxylic Acid Dimethyl Ester (3e). Yellow prisms. mp 171−174 °C (EtOH). IR (KBr) cm^{-1}: 1680 (enone C═O. ^1H NMR (500 MHz; $CDCl_3$) δ (ppm): 2.23 (1H, t, J = 2.4 Hz, −C≡C*H*), 3.03, 3.85 (3H, s, −OMe × 2), 3.88 (1H, dd, J = 16.5, 3.1 Hz, N−CH_2), 3.96 (1H, dd, J = 16.5, 2.4 Hz, N−CH_2), 4.24 (1H, d, J = 11.0 Hz, 4-H), 4.32 (1H, dd, J = 11.0, 2.0 Hz, 4-H), 6.47 (1H, s, 5-H), 7.02−7.83 (9H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 39.9, 51.3, 52.3 (OMe × 2), 58.7 (−*C*H_2−C≡CH), 66.2 (C9c), 71.7 (−*C*≡CH), 78.4 (C2a), 80.3 (−C≡C*H*), 128.4 (C4a), 120.8 (C5), 127.4, 127.5, 128.0, 129.2 and 132.1 (aromatic C), 133.8, 136.9, 145.2, 162.6 and 168.2 (−*C*OO), 178.3 (C9b) and 196.1 (C═O). *m*/*z* (EI) 439 (M^+). The structure was confirmed by the X-ray analysis.

Products from the Reaction of 1a with 1,1-Diethyl-2-propynylamine (2f). 2,2-Diethyl-3-methylene-4-oxo-6,6a-diphenyl-2,3,4,6a-tetrahydro-(3aa,6aa)-1*H*-cyclopenta-[*b*]pyrrole-3a,5-dicarboxylic Acid Dimethyl Ester (5f). Colorless powder. mp 110 °C. IR (KBr) cm^{-1}: 1620, 1744 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.47 (3H, t, J = 7.3, 7.4 Hz, C2−CH_2−CH_3), 1.04 (3H, t, J = 7.3 Hz, J = 7.3 Hz, C2−CH_2−CH_3), 1.46 (2H, m, C2−CH_2−CH_3), 1.61−1.82 (2H, m, C2−CH_2−CH_3), 2.27 (1H, m, N*H*), 3.03 (C3a-3H, s, COOCH_3), 3.81 (3H, s, C5−COOCH_3), 5.08 (1H, s, ═CH), 5.48 (1H, s, ═CH), 7.17−7.67 (10H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 8.56 (C2−CH_2−*C*H_3 × 2), 31.8 (C2−*C*H_2−CH_3), 34.8 (C2−*C*H_2−CH_3), 51.6 (C5−COO*C*H_3), 52.5 (C3a−COO*C*H_3), 127.1, 127.9, 128.3, 128.7, 129.0, 129.7, 129.9, 131.1 (Ar−C), 131.5, 132.0, 139.9 (quaternary C), 150.6 (C3), 164.5 (C5-*C*OO), 168.7 (C3a-*C*OO), 174.5 (C6), 194.8 (C═O). *m*/*z* (EI) 458 (M^+−1). Anal. Calcd. for $C_{28}H_{29}NO_5$: C, 73.18; H, 6.36; N, 3.05. Found: C, 72.52; H, 6.32; N, 2.96.

4,4-Diethyl-2-oxo-9c-phenyl-2,3,4,9c-tetrahydro-(2aa,-9ca)-3-aza-pentaleno[1,6-*ab*]naphthalene-1,2a-dicarboxylic Acid Dimethyl Ester (3f). Yellow powder. mp 155−156 °C. IR (KBr) cm^{-1}: 1630, 1720 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.86 (3H, t, J = 6.7, 7.3 Hz, C4−CH_2−CH_3), 1.11 (3H, t, J = 7.3 Hz, C4−CH_2−CH_3), 1.62−1,78 (2H, m, C4−CH_2−CH_3), 1.90−2.14 (2H, m, C4−CH_2−CH_3), 3.24 (3H, s, C2a−COOCH_3), 3.85 (3H, s, C1−COOCH_3), 6.17 (1H, s, 5-H), 7.02−7.73 (8H, m, Ar−H), 7.74 (1H, d, J = 7.9 Hz, 9-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 8.1 (C4−CH_2−*C*H_3), 9.4 (C4−CH_2−*C*H_3), 31.2 (C4−*C*H_2−CH_3), 52.1 (C1−COO*C*H_3), 52.4 (C2a−COO*C*H_3), 60.4 (C4), 66.5 (C9c), 77.6 (C2a), 122.9 (C5), 127.3, 127.4, 127.6, 127.8, 128.5, 129.0, 131.7 (Ar−C), 129.1, 130.3, 134.5, 137.3 (quaternary C), 162.7 (C1-*C*OO), 171.5 (C2a-*C*OO), 181.1 (C9b), 200.1 (C═O). *m*/*z* (EI) 456 (M^+ − 1). Anal. Calcd. for $C_{28}H_{27}NO_5$: C, 73.51; H, 5.95; N, 3.06. Found: C, 72.38; H, 5.93; N, 2.48.

Products from the Reaction of 1a with 1-Ethynylcyclohexylamine (2 g). Spiro[cyclohexane-1′,4-(2-oxo-9c-phenyl-2,3,4,9c-tetrahydro-(2aa,9ca)-3-aza-pentaleno[1,6-*ab*]naphthalene)-1,2a-dicarboxylic Acid Dimethyl Ester (3 g). Yellow powder. mp 130−132 °C. IR (KBr) cm^{-1}: 1624, 1724 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.32−2.26 (10H, m, spiro methylenes), 3.26 (3H, s, C2a-COOCH_3), 3.84 (3H, s, C1−COOCH_3), 6.33 (1H, s, 5-H), 7.01−7.35 (8H, m, Ar−H), 7.74 (1H d, J = 7.3 Hz, 9-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 22.9, 25.0, 39.6, 40.5 (spiro carbons), 52.0 (C1−COO*C*H_3), 52.3 (C2a−COO*C*H_3), 66.3, (C9c), 77.4 (C2a), 120.3 (C5), 127.2, 127.3, 127.4, 127.8, 128.7, 129.0, 131.8 (Ar−C), 126.8, 129.1, 134.4, 136.9 (quaternary C), 162.6 (C1−*C*OO), 171.5 (C2a−*C*OO), 181.9 (C9b), 200.2 (C═O). *m*/*z* (EI) 469 (M^+). HRMS Calcd. for $C_{29}H_{27}NO_5$ (M^+): 469.1889. Found: 469.2012.

Spiro[cyclohexane-1′,4-(−3-methylene-4-oxo-6,6a-diphenyl-2,3,4,6a-tetrahydro-(3aa,6aa)-1*H*-cyclopenta[*b*]pyrrole)]-3a,5-dicarboxylic Acid Dimethylester (5 g). Yellow powder. mp 160−163 °C. IR (KBr) cm^{-1}: 1606, 1722 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.65−2.04 (10H, m, spiro methylenes), 2.54 (1H, s, N*H*), 3.08 (3H, s, C3a-COOCH_3), 3.80 (3H, s, C5−COOCH_3), 5.17 (1H, s, ═CH), 5.44 (1H, s, ═CH), 7.17−7.65 (10H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 22.9, 25.0, 39.6, 40.5 (spiro carbons), 51.8 (C5−COO*C*H_3), 52.5 (C3a−COO*C*H_3), 74.2 (C6a), 126.9, 128.4, 128.7, 129.5, 130.9 (Aromatic C), 131.5, 132.1, 139.2 (quaternary C), 154.1 (C3), 164.3 (C5−*C*OO), 168.5 (C3a-*C*OO), 174.2 (C6), 194.1 (C═O). *m*/*z* (EI) 471 (M^+). Anal. Calcd. for $C_{29}H_{29}NO_5$: C, 73.87; H, 6.20; N, 2.97. Found: C, 73.65; H, 6.22; N, 2.93.

Product from the Reaction of 1a with 2-Propyn-1-ol (2h). 3-Methylene-4-oxo-6,6a-diphenyl-2,3,4,6a-tetrahydro-(3aa,6aa)-cyclopenta[b]furan-3a,5-dicarboxylic Acid Dimethyl Ester (10). Colorless prisms. mp 84−85 °C. IR (KBr) cm^{-1}: 1606, 1742 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.11 (3H, s, C3a-COOCH_3), 3.84 (3H, s, C5−COOCH_3), 4.55 (1H, d, J = 13.4 Hz, 2-H), 4.90 (1H, d, J = 13.4 Hz, 2-H), 5.32 (1H, s, ═CH), 5.44 (1H, s, ═CH), 7.25−7.43 (10H, m, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.0 (C5−COO*C*H_3), 52.6 (C3a-COO*C*H_3), 60.3 (C2), 73.7 (C6a), 111.4 (═CH_2), 126.7, 127.7, 128.5, 128.6, 130.9 (Aromatic C), 131.2, 134.5, 137.2 (quaternary C), 143.3 (C3), 164.0 (C5-*C*OO), 167.5 (C3a-*C*OO), 168.2 (C6), 192.1 (C═O). *m*/*z* (FAB) 405 (M^++1). Anal. Calcd. for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.13; H, 5.05.

The Diels−Alder Adduct (**9**) is found in the reaction mixture. Yellow oil. IR (Nujol) cm^{-1}: 1774 (C═O, COO). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.85 (1H, s, O*H*), 3.54 (3H, s, C−COOCH_3), 3.79 (3H, s, C−COOCH_3), 4.72 (2H, d, J = 6.1 Hz, CH_2), 6.93−7.44 (10H, m, Ar−H), 7.89 (1H, s, ═C−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.0 (C−COO*C*H_3), 52.5 (C−COO*C*H_3), 63.2 (>CH_2), 77.0 (CO−*C*−CO), 77.3 (CO-*C*-CO), 129.7 (H−C═), 126.7, 126.9, 127.2, 127.3, 128.2, 129.7, 129.9 (Aromatic C), 137.7, 138.0, 138.3, 140.6 (quaternary C), 168.3 (C−*C*OO), 169.5 (C−*C*OO), 192.0 (C═O). *m*/*z* (FAB) 403 (M^+ − 1).

Reaction of 1a with Aniline.[3] A mixture of **1a** (0.5 g, 1.4 mmol) and aniline (0.3 g, 3.2 mmol) in acetonitrile (2 mL) was stirred in an ice−water bath for 3h. After evaporation of the solvent, the residue was chromatographed on silica gel using benzene/AcOEt = 20:1 to give the 1,5 sigmatropic rearrangement product **7** (581 mg, 90%) and the crude 1,4 adduct **6** (72 mg, 10%).

6: Yellow powder (crude). IR (KBr) cm^{-1} : 3368 (>NH), 1716 (C═O); ^1H NMR ($CDCl_3$) δ (ppm): 3.62 (3H, s, C2−COOMe), 3.82 (3H, s, C5−COOMe), 7.04−7.41 (15H, m, Ar−H). ^{13}C NMR ($CDCl_3$) δ (ppm): 52.5, 52.6 (COO*C*H_3 × 2), 53.9 (═CH), 59.0 (>C(NH−Ph)C−OOCH_3), 144.5(>C═*C*−COOCH_3), 163.5-(C═CPh), 169.6, 178.3, 195.1 (>C═O).

7: Yellow prisms. mp 175°. IR (KBr) cm^{-1}: 3368 (>NH), 1774, 1732, 1712 (C═O). ^1H NMR ($CDCl_3$) δ (ppm): 3.38 (3H, s, C2−COOCH_3), 3.90 (3H, s, C5−COOCH_3), 5.29 (1H, s, methine), 5.40 (1H, s, NH), 6.59−7.40 (15H, m, Ar−H). ^{13}C NMR ($CDCl_3$) δ (ppm): 52.0, 52.5 (COO*C*H_3 × 2), 52.8 (>CH−), 75.0 (>*C*(NH−Ph)COOCH_3), 142.6 (>C═*C*−COOCH_3), 164.4 (C═*C*−Ph), 167.8, 170.3, 196.0 (>C═O). *m*/*z* (EI) 441 (M^+). The structure was confirmed by the X-ray analysis.[9]

Single-Crystal X-ray Analyses of the Products. Molecular Structure of 3a. Single crystals of the compound **3a** were prepared by slow evaporation of an ethanol solution at room temperature. The cell constants were found by a least-squares procedure using the values of the Bragg angles of 20 reflections. Systematic absences of reflections indicate the space group to be $P2_1/n$, a nonstandard setting of $P2_1/c$ (no. 14).

All measurements were made on a Rigaku AFC-6 four-circle autodiffractometer with a graphite monochromated Mo Kα radiation. The reflection data were collected using $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. Of the unique reflections measured, reflections having $Io > 3.00\sigma I$ were used. The structures were solved by direct method.[12] The non-

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hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. Some hydrogens of the methoxycarbonyl groups were located on the calculated positions and refined. The block-diagonal least-squares refinement was used and the unweighted (R) and weighted agreement factors (R_w) are given.

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography.[13] All calculations were performed on a S4−2 workstation with *UNICS III* Crystal Structure Analysis Package.[14]

Data collection and refinement parameters for **3a**. Formula $C_{27}H_{25}O_5N$, crystal system monoclinic, space group $P2_1/n$, a = 14.022(4), b = 13.823(7), c = 11.754(7) Å, β = 94.21(3)°, V = 2272(2) Å^3, Z = 4, D_c = 1.297 gcm^{-3}, radiation Mo K$_\alpha$ (λ = 0.71069 Å, scan range 2θ < 55.0°, unique data collected 4359, unique data used ($I > 3.00\sigma(I)$) 2576, R = 0.072, R_w = 0.096.

The atomic coordinates, distances, and angles are listed in Table S1−S4.

Molecular Structure of 4b. Single crystals were prepared by slow evaporation of a methanol solution at room temperature. All measurements were made on a Rigaku AFC7R four-circle autodiffractometer with a graphite monochromated Mo K$_\alpha$ radiation (λ = 0.7107 Å) and a rotating anode generator. The crystal structure determination of **4b** was performed by essentially the same manner described in **3a**. After adding the hydrogen atoms, keeping their vibrational amplitude fixed (B(H) = B(C) + 1.0 Å), and refining the values with anisotropic temperature factors for all C, N, and O atoms, the full-matrix least-squares refinements were performed. All calculations were performed on a Silicon Graphics IRIS Indigo workstation with *teXsan* Crystal Structure Analysis Package.[14b,15] The result is summarized in Tables S5−S8.

Data collection and refinement parameters for **4b**. Formula $C_{28}H_{31}NO_6$, crystal system orthorhombic, space group $P2_12_12_1$-(#19), a = 14.61(1), b = 18.83(1), c = 9.292(8) Å, V = 2557(3) Å^3, Z = 4, D_c = 1.240 gcm^{-3}, D_m = 1.158(*aq*. KI) gcm^{-3}, radiation Mo K$_\alpha$ (λ = 0.71069 Å, scan range 2θ < 55.0°, unique data collected 7220, unique data used ($I > 3.00\sigma(I)$) 3070, R = 0.05, R_w = 0.042.

Molecular Structure of 5c. Single crystals were prepared by slow evaporation of an ethanol-ethyl acetate solution at room temperature. The crystal structure determination of **5c** was performed by essentially the same manner described in **4b**. Data collection and refinement parameters for **5c**. Formula $C_{24}H_{21}NO_5$, crystal system monoclinic, space group, $P21/n$, a = 8.901 (2), b = 11.392 (3), c = 21.125 (2) Å, β = 94.32(1)°, V = 2135.9(7) Å^3, Z = 4, D_c = 1.254 gcm^{-3}, D_m = 1.280(aq. KI) gcm^{-3}, radiation Mo K$_\alpha$ (λ = 0.71069 Å, scan range 2θ < 55.0°, unique data collected 4910, unique data used ($I > 3.00\sigma(I)$) 3519, R = 0.063, Rw = 0.093.

The results are listed in Tables S9−S12.

Molecular Structure of 3e. Single crystals were prepared by slow evaporation of an ethanol solution at room temperature. The crystal structure determination of **3e** was performed by essentially the same manner described in **4b**. At the final stage of the refinement, four peaks appeared in the difference Fourier map. Those were tentatively assigned to water oxygens with a multiplicity of 0.5 and included in the further refinement. In light of the quality of R facter, the space group of $P\bar{1}$(#2) was selected.

Data collection and refinement parameters for **3e**. Formula $C_{27}H_{22}NO_5{\cdot}2H_2O$, crystal system triclinic, space group $P1(-)$-(#2), a = 9.848(2), b = 13.201(2), c = 9.540(2)Å, α = 96.94(2), β = 107.77(2)°, γ = 92.66(1)°, V = 1167.9(4) Å^3, Z = 2, D_c = 1.348 gcm^{-3}, D_m = 1.352(aq. KI) gcm^{-3}, radiation Mo K$_\alpha$ (λ = 0.71069 Å, scan range 2θ < 55.0°, unique data collected 5359, unique data used ($I > 3.00\sigma(I)$) 3506, R = 0.075, R_w = 0.073.

The results are listed in Tables S13−S16.

Molecular Orbital Calculation. Semiempirical MO calculations were run through the ANCHOR II interface using MOPAC6.0[5] on a Fujitsu S4/2 workstation (WS) or through the CS Chem3D Pro interface using MOPAC97 on a Macintosh G3 personal computer. The ab initio and DFT computations[3] were carried out on a Scientists' Paradise Dragon AXP5A/433 computer or a HP Exemplar Technical Server TS VS2550 KS in the Kumamoto University Information Processing Center.

The ground states (GS) were optimized by the EF routine implemented in the MOPAC program packages using MNDO−PM3 (PM3) approximation.[5a] The transition states (TS) were located by the transition-state location routine.

The fully optimized geometries calculated by AM1 or PM3 method were used as starting geometries for the ab initio and DFT calculations. Graphical analysis of the MO calculation data was performed on a Macintosh G3 personal computer.

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Supporting Information Available: X-ray crystal reports for **3a**, **4b**, **5c**, and **3e** and MO calculation data. This material is available free charge via the Internet at http://pubs.acs.org. This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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