PARTICIPATION OF SUPERJACENT AND SUBJACENT ORBITALS FOR THE CYCLOADDITION REACTION OF 2<u>H</u>-4,9-METHANOCYCLOUNDECA[<u>b</u>]FURAN-2-ONE WITH ELECTRON-DEFICIENT DIENOPHILES

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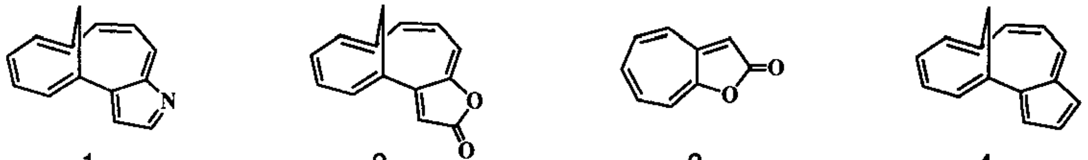
Abstract--Cycloaddition reactions of 2H-4,9-methanocycloundeca[b]furan-2-one with dimethyl acetylenedicarboxylate (DMAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) were studied. The former reaction underwent a [12+2] cycloaddition, but the latter, only a [4+2] and a plausible [12+2] cycloadditions. The similar reaction of 2H-cyclohepta[b]furan-2-one with DMAD underwent a [4+2] and an [8+2] cycloadditions in a ratio of 8 : 1, while that with PTAD, only [4+2] cycloaddition. The periselectivity of the reactions was discussed on the basis of the MNDO calculations.

INTRODUCTION

Recently we have engaged in the synthesis and structural properties of 1-aza-4,9-methanocyclopentacycloundecene (1) and its isomers.[1] In connection with the study, we previously prepared 2H-4,9-methanocycloundeca[b]furan-2-one (2) through cycloaddition of 3,8-methano[11]annulenone[2] with dichloroketene followed by reductive elimination of the chlorine atom.[3] Since 2H-cyclohepta[b]furan-2-one (3)[4] has been used for the



1 2 3 4

Scheme 1

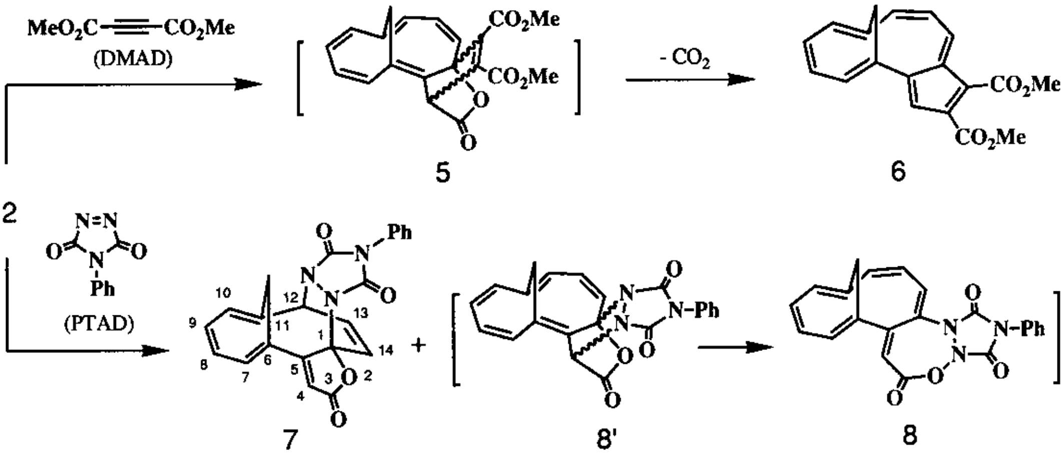
preparation of versatile azulene derivatives by the formal [8+2] cycloadditions with enamines,[5] vinyl-ethers[6] and its analogues,[7] ketene acetals,[8] and furans,[9] the compound (2), which is a vinylogue of 3, is expected to be a precursor of novel 4,9-methanocyclopentacycloundecene (4).

The reaction of 3 and its derivatives with the dienophile, which has a low lying LUMO, has been reported to give [4+2]-adducts exclusively. The periselectivity concerning [4+2] and [8+2] has been rationalized on the basis of the consideration of superjacent and subjacent orbitals based on MO calculations.[10] Thus we studied the reaction of 2 and 3 with the dienophiles, dimethyl acetylenedicarboxylate (DMAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). We will describe here the results including rationalization of the periselectivity based on the MNDO calculations, which predicted the importance of superjacent and subjacent orbitals.

RESULTS AND DISCUSSION

The reaction of 2 with three molar equivalent amounts of DMAD was heated under reflux in o-xylene to give novel 1,2-bis(methoxycarbonyl)-4,9-methanocyclopentacycloundecene (6) in 1% yield, in addition to 52% of unreacted 2. The compound 6 was probably derived from the initial [12+2] cycloaddition giving 5 followed by decarboxylation. When the reaction of 2 with excess amount of DMAD was carried out until 2 disappeared, the product (6) was decomposed completely by prolonged heating. However the reaction did not proceed under reflux in toluene, and unreacted 2 was recovered quantitatively. Thus the product (6) as well as the expected [4+2]-adduct seems to be unstable under the reaction conditions in refluxing o-xylene. So we carried out the reaction of 2 with more reactive dienophile under mild conditions. Compound (2) reacted with PTAD[11] in benzene at room temperature to give a [4+2]-adduct (7) and an unidentified adduct (8) in 66% and 8% yields, respectively.

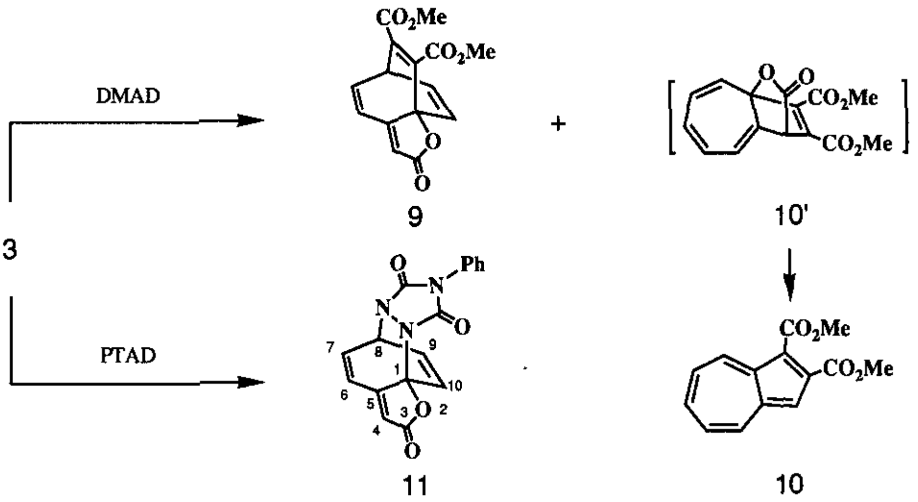
The structural assignment of 6 and 7 was made on the basis of high ms, ir, and ^{1}H-nmr spectra, all of which are consistent with the proposed structures (numbering of 7 in a convenient manner is shown in Scheme 2). Especially the chemical shifts and the coupling constants suggest that 6 is aromatic compound and its spectral data are also



Scheme 2

similar to those of 5,10-methanocyclopentacycloundecene derivatives,[12] which are suggested to be vinylogues of azulene based on the spectral data. On the other hand, the ^{1}H-nmr spectral data clearly suggested that 7 is a [4+2]-adduct. Furthermore the signal of one of the methylene-protons of 7 appears at low-field (δ 3.77). This type of behavior has not been observed in the endo-adduct (anti to the methylene bridge) of 1,6-methano[10]annulene with PTAD.[13] Thus one of the methylene-proton is suggested to be close to the nitrogen atom, and the stereochemistry of 7 was assigned as depicted in the structural formula (7). The compound (8) is a 1:1 adduct of 2 with PTAD, but the ^{1}H-nmr spectral data did not seem to explain the expected [12+2]-adduct (8') (Scheme 2) as well as the stereoisomers of 7. However, the ^{1}H-chemical shifts of 8 are similar to those of 2,[3] and the ms spectrum of 8 exhibited the m/z value of 252 (2 + N=C=O)$^+$, which is not observed in the ms spectrum of 7. Furthermore, the electronic spectra of 8 and 2 similar to each other, suggesting the existence of a similar chromophore in both compounds. Thus the structure of 8 was tentatively proposed as depicted in Scheme 2, and 8 would be derived by a rearrangement of the [12+2]-adduct (8').

On the other hand, the reaction of 3 with excess amount of DMAD was carried out under reflux in o-xylene to give a [4+2]-adduct (9)[10] and azulene derivative (10)[14] in a ratio of 8 : 1. The compound (10) is probably derived from [8+2] cycloaddition followed by



Scheme 3

decarboxylation as in the case of 6. The reaction of 3 with PTAD at room temperature afforded a [4+2]-adduct (11) in a 66% yield as a single product (Scheme 3). The compounds (9) and (10) have been known, and the structures were determined on the basis of the comparison of the spectral data with those reported in the literature.[10,14] The structure of 11 was also easily deduced on the basis of the spectral data as well as comparison of the ^{1}H-nmr spectrum (numbering of 11 in a convenient manner is shown in Scheme 3) with those of 9 and its derivatives.[10] The stereochemistry of 11 was deduced from a secondary orbital interaction between C-7 and C-8 of 3 and the carbonyl carbon atoms of PTAD.

MOLECULAR ORBITAL CONSIDERATIONS

As mentioned above, the reaction of nonalternant aromatic compound (3) with DMAD gave the [4+2]- and [8+2]-adducts, whereas 3 with PTAD gave only [4+2]-adduct. Although the reaction of 2, which is a vinylogue of 3, with DMAD gave no [4+2]-adduct but only [12+2]-adduct in low yield, 2 reacted with PTAD to give a [4+2]-adduct and a plausible [12+2]-adduct. Thus the reactivities of 2 and 3 are similar to each other. No formation of the possible [4+2]-adduct in the reaction of 2 with DMAD is probably due to instability of the constrained structure of the product.

The molecular orbitals of 2, 3, DMAD, and PTAD were calculated by the MNDO method

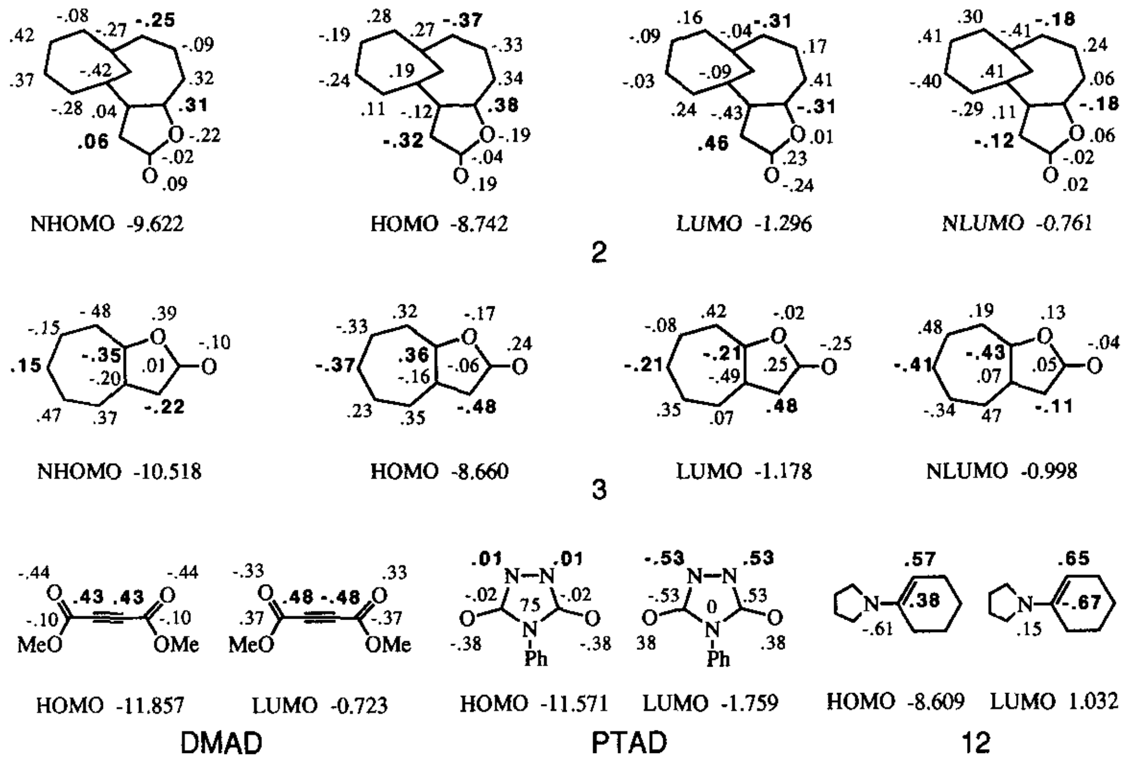


Figure 1. Coefficients and energy levels of molecular orbitals of **2**, **3**, **DMAD**, **PTAD**, and **12**.

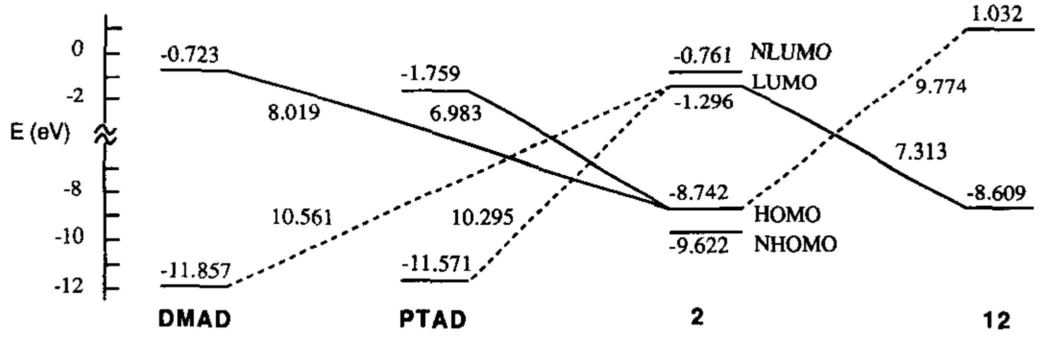


Figure 2. Calculated Orbital Energies and Energy Separations of **2** and Dienophiles.

together with 1-(1-pyrrolidinyl)cyclohexene (12) (Figure 1).[16] Considering the energy separation between the frontier orbitals,[16] the formation of both [4+2]- and [12+2]-adducts are symmetry allowed for the reactions of 2 with DMAD and PTAD [HOMO(2)-LUMO(DMAD and PTAD) interactions], respectively, whereas the formation of a [4+2]-adduct is allowed [LUMO(2)-HOMO(12) interaction] for the reaction of 2 with enamine (12) (Figures 1 and 2). Similarly, the formation of both [4+2]- and [8+2]-adducts are allowed [HOMO(3)-LUMO(DMAD and PTAD) interaction] for the reaction of 3 with DMAD and PTAD. However, these are not satisfactory to explain the experimental results in details.

Since both pairs of HOMO and NHOMO and LUMO and NLUMO have the same pseudosymmetries at C-10 and C-12a for 2 and C-6 and C-8a for 3, the participation of subjacent and superjacent orbitals would become important for the periselectivity of the cycloadditions. Paddon-Row and his co-workers have pointed out that the superjacent orbital-effects are important to explain the periselectivity for cycloaddition reactions of nonalternant hydrocarbon, 6,6-dimethylfulvene with cyclopentadiene.[17] Takeshita and his co-workers have also rationalized the reactions of 3 and its derivatives with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[3.2.1]heptadiene (13) giving only [4+2]-adducts by the participation of subjacent and superjacent-orbital interactions.[10]

The preferential formation of [4+2]-adducts (except in the reaction of 2 with DMAD) over [12+2]-adduct (or [8+2]-adduct) in the reaction of 2 (or 3) with DMAD and PTAD is consistent with the prediction from the square of the sum of the products of the coefficients of interacting centers.[17] Considering only the HOMO(2 or dienophile)-LUMO(dienophile or 2) interactions, the stabilization energies (ΔE) of the [4+2] cycloaddition is slightly larger than that of the [12+2] cycloaddition ([4+2]/[12+2] = 230/143 for DMAD; 222/196 for PTAD) (Table 1). However, when the subjacent and superjacent orbital effects are considered, the total stabilization energies of the [4+2] cycloaddition becomes larger in much extent than that of the [12+2] cycloaddition ([4+2]/[12+2] = 332/158 for DMAD; 330/196 for PTAD) (Table 1). Thus the [4+2] addition

Table 1. Calculated Stabilization Energy (ΔE) between **2** and Dienophiles (x 10^{-4} β^2).

2	Dienophiles	ΔE (between **2** and **DMAD**)		ΔE (between **2** and **PTAD**)	
		[4+2]	[12+2]	[4+2]	[12+2]
NLUMO	HOMO	22	15	≈0	≈0
LUMO	HOMO	68	—	≈0	—
HOMO	LUMO	162	143	222	196
NHOMO	LUMO	80	—	108	—
Total		332	158	330	196

Table 2. Calculated Stabilization Energy (ΔE) between **3** and Dienophiles (x $10^{-4}\ \beta^2$).

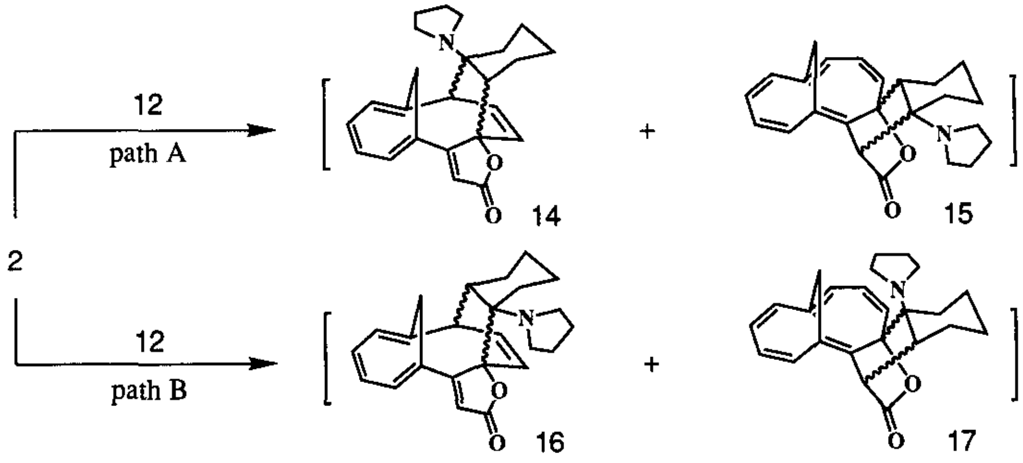
3	Dieno-philes	ΔE (between **3** and **DMAD**)		ΔE (between **3** and **PTAD**)	
		[4+2]	[8+2]	[4+2]	[8+2]
NLUMO	HOMO	120	67	≈0	≈0
LUMO	HOMO	31	—	≈0	—
HOMO	LUMO	155	209	217	293
NHOMO	LUMO	68	—	93	—
Total		374	276	310	293

reaction predominates over the [12+2] cycloaddition in the case of the reaction of **2** with **DMAD** and **PTAD**. However, a [4+2]-adduct of **2** with **DMAD** would be decomposed under reaction conditions. In the case of the reactions of **3** with **DMAD** and **PTAD**, HOMO(**3** or dienophile)-LUMO(dienophile or **3**) interactions predicted the preferential formation of the [8+2]-adducts ([4+2]/[8+2] = 186/209 for **DMAD**; 217/293 for **PTAD**) (Table 2). On the contrary, the total stabilization energy of the [4+2] cycloaddition becomes more favorable than the [8+2] cycloaddition based on the consideration of the effects of subjacent and superjacent orbital-interactions ([4+2]/[8+2] = 374/276 for **DMAD**; 310/293 for **PTAD**) (Table 2), as in the cases of the reaction of **3** and its derivatives with **13**.[10] Thus the preferential formation of the [4+2]-adducts in the reaction of **2** and **3** with **DMAD** as well as **PTAD** was rationalized.

On the other hand, the reaction of **3** with enamines as well as electron-donating dienophiles has been clarified to give versatile azulenes via the formal [8+2]-adducts.[5-9] The HOMO-LUMO interactions and an involvement of NHOMO and NLUMO effects favored the

Table 3. Calculated Stabilization Energy (ΔE) between **2** and **12** (x $10^{-4}\ \beta^2$).

2	12	ΔE_A		ΔE_B	
		[4+2]	[12+2]	[4+2]	[12+2]
NLUMO	HOMO	39	32	40	23
LUMO	HOMO	124	—	125	—
HOMO	LUMO	244	219	250	222
NHOMO	LUMO	125	—	127	—
Total		532	251	542	245



Scheme 4

formation of [4+2]-adduct.[10] Therefore there still remained whether the [8+2] cycloaddition is really kinetically-controlled process in the formation of azulenes.

In the reaction of 2 with enamine (12), the calculated stabilization energies for the pathway A (ΔE_A) and the pathway B (ΔE_B) in Scheme 4 are also shown in Table 3. The results predict that the HOMO(2 or 12)-LUMO(12 or 2) interaction favors the formation of a [4+2]-adduct slightly, whereas an involvement of NHOMO and NLUMO effects also resulted in the formation of a [4+2]-adduct in more extent. The attempted reaction of 2 with 12, however, gave only tarry materials and no adduct was identified.

In conclusion, the compound (3) is a valuable synthone for the preparation of versatile azulenes in the formal [8+2] cycloaddition in a synthetic aspect. Thus further reaction of 2 with several kinds of enamines are now underway in a view of the synthesis of azulene vinylogues in due course.

EXPERIMENTAL

^{1}H- and ^{13}C-nmr spectra were recorded on a Hitachi R-90H, JEOL JNM-GSX400, and GE-Omega 500 spectrometers in CDCl$_3$, and chemical shifts were given in ppm (δ) relative to internal SiMe$_4$ standard. Ir spectra were recorded on a Perkin-Elmer 1640 spectrophotometer. Uv spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. Mass spectral studies and high-resolution mass spectral studies were conducted by using a Shimadzu

GCMS QP-1000 and a JEOL JMS-DX300 spectrometers. Microanalyses were performed at the Materials Characterization Central Laboratory of Waseda University. Mps were recorded on a Buchi apparatus and are uncorrected. All cycloadditions were performed under a dry nitrogen atmosphere.

Reaction of 2 and DMAD. A solution of 1 (100 mg, 0.48 mmol) and DMAD (70 mg, 0.63 mmol) in *o*-xylene (1 ml) was heated under reflux for 3 h. After removal of the solvent, the residue was purified by tlc on alumina (hexane/diethyl ether: 3/1) to give 6 (2 mg, 1%) and unreacted 2 (52 mg, 52%). 6: green oil; ^{1}H-nmr (500 MHz) δ 0.11 (1H, d, J=11.7 Hz, bridge H-*Z*), 0.26 (1H, d, J=11.7 Hz, bridge H-*E*), 3.97 (3H, s, $-OCH_3$), 3.98 (3H, s, $-OCH_3$), 7.27 (1H, dd, J=11.7, 9.2 Hz, H-11), 7.30 (1H, dd, J=9.5, 9.2 Hz, H-7), 7.59 (1H, t, J=9.5 Hz, H-6), 7.62 (1H, d, J=9.2 Hz, H-8), 7.73 (1H, d, J=9.2 Hz, H-10), 7.93 (1H, s, H-3), 8.19 (1H, d, J=9.5 Hz, H-5), 9.26 (1H, d, J=11.7 Hz, H-12); ir ($CHCl_3$) 1717 cm^{-1}; ms (m/z) 309 ($[M+1]^+$ 21%), 308 (M^+, 93), 189 (100); uv λ_{max}(in hexane, log ε) 257 (4.14), 300 (4.26), 369 (4.47), 434 (3.74), 684 (2.96) nm; (in EtOH, log ε) 254 (4.18), 300 (4.27), 365 (4.50), 433 (3.70), 713 (2.92) nm. High ms Calcd for $C_{19}H_{16}O_4$: *308.1048. Found: 308.1072.*

Reaction of 2 and PTAD. To a solution of 2 (63 mg, 0.3 mmol) in benzene (5 ml) was added a solution of PTAD (50 mg, 0.3 mmol) in benzene (5 ml). The reaction mixture was stirred at room temperature for 48 h, and the orange precipitates were collected by filtration and washed with benzene. Recrystallization of the precipitates from acetonitrile gave 7 (76 mg, 66%), and the filtrate was recrystallized from MeOH to give 8 (9 mg, 8%). 7: colorless needles; mp 237 °C (decomp.); ^{1}H-nmr (500 MHz) δ 0.97 (1H, d, J=12.4 Hz, bridge H-*E*), 3.77 (1H, ddd, J=12.4, 1.4, 1.1 Hz, bridge H-*Z*), 5.84 (1H, dd, J=7.4, 1.4 Hz, H-12), 6.26 (1H, s, H-4), 6.33 (1H, d, J=9.9 Hz, H-14), 6.52 (1H, dd, J=5.5, 1.1 Hz, H-10), 6.82 (1H, d, J=5.5 Hz, H-7), 6.89(1H, dd, J=11.0, 5.5 Hz, H-9), 6.90 (1H, dd, J=9.9, 7.4 Hz, H-13), 7.01 (1H, dd, J=11.0, 5.5 Hz, H-8), 7.11 (2H, dm, J=7.0 Hz, Ph), 7.35 (1H, tm, J=7.3 Hz, Ph), 7.39 (2H, ddm, J=7.3, 7.0 Hz, Ph); ^{13}C-nmr (125 MHz) δ 32.43, 55.91, 114.54, 117.92, 119.94, 124.22, 125.82, 128.39, 128.50, 128.81, 129.31, 130.47, 130.66, 132.97, 134.22, 147.00, 152.97, 159.86, 168.89 (three carbons are overlapping); ir ($CHCl_3$) 1770 and 1720 cm^{-1}; ms (m/z) 386 ($[M+1]^+$, 34%), 385 (M^+, 60), 210 (100).

Anal. Calcd for $C_{22}H_{15}N_3O_4$: C, 68.57; H, 3.92; N, 10.90. Found: C, 68.6; H, 3.8; N, 10.9. 8: red powder; mp 205 °C (decomp. from MeOH); ^{1}H-nmr (500 MHz) δ 0.68 (1H, d, J=12.2 Hz, bridge H), 2.04 (1H, d, J=12.2 Hz, bridge H), 6.49 (1H, t, J=11.3 Hz), 7.03-7.06 (2H, m), 7.28-7.39 (5H, m), 7.42 (1H, t, J=7.3 Hz, Ph), 7.51 (2H, t, J=7.3 Hz, Ph), and 7.58 (2H, d, J=7.3 Hz, Ph); ir ($CHCl_3$) 1775 (sh) and 1724 cm^{-1}; uv λ_{max} (in EtOH, log ε) 222 (4.32), 298 (4.09), 450 (3.83) nm; ms (m/z) 385 (M^+, 53%), 252 (18), 210 (100). High ms Calcd for $C_{22}H_{15}N_3O_4$: 385.1063. Found: 385.1043.

Reaction of 3 and DMAD. A solution of 3 (300 mg, 2.05 mmol) and DMAD (860 mg, 6.06 mmol) in o-xylene (2 ml) was heated under reflux for 12 h. To this reaction mixture was added DMAD (446 mg, 3.14 mmol), and the mixture was refluxed for another 5 h. Furthermore, to the reaction mixture was added DMAD (153 mg, 1.08 mmol), and the mixture was refluxed for 14 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt: 3/1) to give 9[10] (420 mg, 71%) and 10[14] (20 mg, 9%). 9: colorless plates; mp 118-119 °C (from MeOH) (lit.,[10] 121-123 °C); ^{1}H-nmr (90 MHz) δ 3.78 (3H, s), 3.82 (3H, s), 4.50 (1H, dd, J=7.8, 6.8 Hz), 5.84 (1H, s), 6.15 (1H, d, J=10.1 Hz), 6.37 (1H, dd, J=7.8, 1.5 Hz), 6.53-6.74 (2H, m). 10: violet oil; ^{1}H-nmr (90MHz) δ 3.95 (3H, s), 3.98 (3H, s), 7.47 (1H, s), 7.44-7.88 (3H, m), 8.47 (1H, d, J=9.5 Hz), 9.41 (1H, d, J=9.9 Hz).

Reaction of 3 and PTAD. To a solution of 3 (58.4 mg, 0.4 mmol) in toluene (4 ml) was added a solution of PTAD (70 mg, 0.4 mmol) in toluene (8 ml). After the reaction mixture was stirred at room temperature for 48 h, the orange precipitates were collected by filtration and washed with benzene. Recrystallization of the collected precipitates from methanol gave 11 (85 mg, 66%). 11: yellow prisms; mp 142 °C (decomp.); ^{1}H-nmr (500 MHz) δ 5.49 (1H, dd, J=7.3, 7.0 Hz, H-8), 6.11 (1H, s, H-4), 6.40 (1H, d, J=9.2 Hz, H-6), 6.60 (1H, d, J=10.1 Hz, H-10), 6.65 (1H, dd, J=10.1, 7.0 Hz, H-9), 6.77 (1H, dd, J=9.2, 7.3 Hz, H-7), 7.37-7.46 (5H, m, Ph); ^{13}C-nmr (100 MHz) δ 52.61, 93.56, 115.24, 123.05, 125.22, 128.65, 129.17, 130.05, 131.02, 135.81, 151.97, 153.58, 154.37, 168.85 (two carbons are overlapping); ir ($CHCl_3$) 1798 and 1723 cm^{-1}; ms (m/z) 321 (M^+, 2%), 146 (100). Anal. Calcd for $C_{17}H_{11}N_3O_4$: C, 63.55; H, 3.45; N, 13.08. Found: C, 62.9; H, 3.4; N, 13.1.

Reaction of 2 with 12. A solution of 2 (50 mg, 0.24 mmol) and 12 (360 mg, 2.4 mmol) in BuOH (3 ml) was heated under reflux for 3 h. After removal of the solvent, the tarry residue was chromatographed on Florisil. The fractions eluted with hexane-AcOEt (3/1) were concentrated and then separated by tlc on alumina (hexane/AcOEt: 3/1) to give only unreacted 2 (10 mg, 20%).

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