Synthetic Photochemistry. XLIX.[1] Synthesis and Photoisomerization of 2-Acetyl-2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one. An MO Explanation of the Cycloaddition of Cyclohepta[*b*]pyrrol-2(1*H*)-ones

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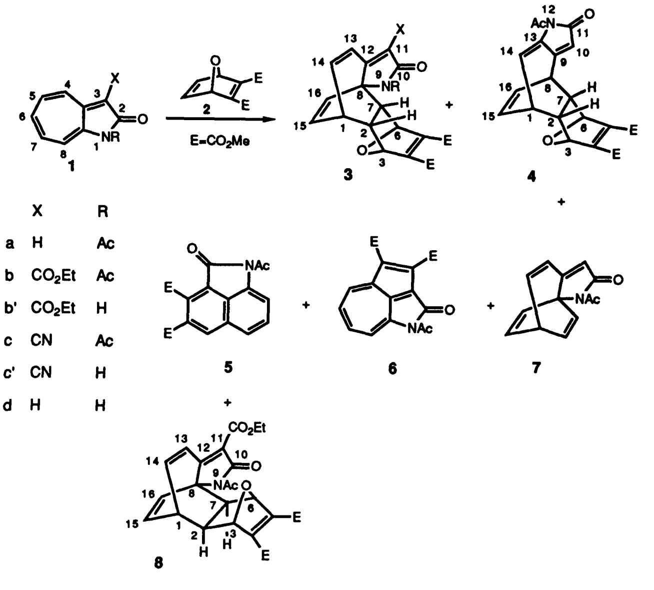
Thermal cycloaddition reactions of 2,3-bis(methoxycarbonyl)-7-oxabicycloheptadiene with cyclohepta[*b*]pyrrol-2(1*H*)-ones gave the [4+2]adducts and products derived from the [8+2]adducts. Among [4+2]adducts, a new adduct was isolated. Cyclohepta[*b*]pyrrol-2(1*H*)-ones, having a substituent at the C-3 position exclusively, gave [4+2]adducts. The photolysis of 2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one afforded substituted 9-methylenebarbaralane, 5-methylenetricyclo[4.3.0.$0^{2,9}$]nonadiene, and 1-methylenedihydroindene derivatives.

Currently, we have been interested in the thermal cycloaddition–cycloreversion process of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene, an acetylene equivalent, with tropones,[2] cyclohepta[*b*]furan-2(2*H*)-ones,[3] and anthracenes.[4] Since this procedure is useful to construct various cage compounds, we have now investigated the reaction with cyclohepta[*b*]pyrrol-2(1*H*)-ones (**1**) to obtain 2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-ones. Although Abe and Takehiro recently showed that the thermal cycloaddition between **1** and dimethyl butynedioate (DMBD) gave the products via a [8+2]cycloaddition,[5] we have now found that the reactions of **1** and 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**2**) under 3000 bar afforded [4+2] and [8+2]adducts. In addition, the photorearrangement of 2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one furnished similar products as in the oxa analogues, 2-oxatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-ones.

Results and Discussion

Cycloaddition Reaction of 1 and 2. When a chlorobenzene solution of 1-acetylcyclohepta[*b*]pyrrol-2(1*H*)-one (**1a**) and **2** was heated at 120 °C under 3000 bar, four products (**3a**, and **4—6**) were formed and isolated via silica-gel chromatography in 12, 4, 8, and 6% yields, respectively (Scheme 1). Products **3a** and **4** were 1:1-cycloadducts, respectively; the ^{1}H NMR spectrum of product **3a** revealed five methine protons with coupling constants ($J_{1,2}=J_{2,3}=J_{6,7}=0$—1.1 Hz), which are very similar to those of endo [4+2]adducts formed by the addition of cyclohepta[*b*]furan-2(2*H*)-ones and **2**.[3] On the other hand, the structure of **4** was deduced to be another endo [4+2]adduct; the ^{1}H NMR spectrum showed the presence of four olefinic and six methine protons with coupling constants ($J_{1,2}=J_{2,3}=$



Scheme 1.

Table 1. Product Distribution of 1 and 2

	Conditions$^{a)}$	Products (Yield/%)
1a	3000, 120, 20, CB,$^{b)}$	**3a** (12), **4** (4), **5** (8), **6** (6),
	1, 130, 20, CB	**5** (16), **7** (13)
1b	3000, 120, 20, anhydrous dioxane	**3b** (26), **8** (6.5)
	3000, 115, 20, dioxane	**3b′** (45)
1c	3000, 120, 20, anhydrous dioxane	**3c** (20), **3c′** (24)
1d	3000, 120, 20, anhydrous dioxane	No reaction$^{c)}$

a) Pressure/bar, temperature/°C, time/h, and solvent. b) Chlorobenzene. c) The reaction of **1d** and DMBD in refluxing acetonitrile gave five products derived from a [8+2]adduct.[5]

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$J_{6,7}=J_{7,8}=0$—1.1 Hz). Additionally, H-14 appeared at δ 7.69 (dd, J=9.5, 1.8 Hz). This signal at the low-field could be explained in terms an α-position to the *N*-acetyl group. These observations were consistent to the structure of **4**. The connectivities of the hydrogens of **3** and **4** were further confirmed by the ^{1}H COSY spectra. Product **5** was the naphthalene derivative, being identical with an authentic sample.[6] Product **6** was assigned as 1-acetyl-3,4-bis(methoxycarbonyl)pyrrolo[4,3,2-*cd*]azulen-2(1*H*)-one by comparing the spectral data with related compounds.[5] The product distributions of **1** and **2** are summarized in Table 1.

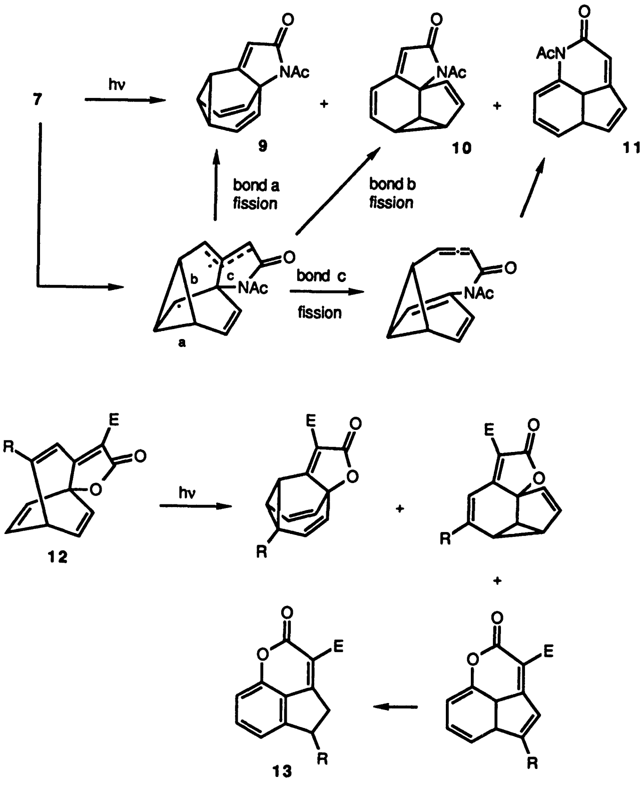
When the reaction between **1a** and **2** was performed at 130 °C in a sealed tube, a new product **7** was obtained in 13% yield together with **5** (16%). Since this new product **7** was also formed together with 3,4-bis(methoxycarbonyl)furan from **3a** by heating at 135 °C and its NMR spectrum indicated to have a symmetry element in a molecule, **7** was assigned to be 2-acetyl-2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one.

The reaction of 1-acetyl-3-ethoxycarbonylcyclohepta[*b*]pyrrol-2(1*H*)-one (**1b**) and **2** in anhydrous dioxane gave a 1:1-adduct (**3b**) and another 1:1-adduct (**8**) together with a deacetylated derivative (**1b′**)[7] of **1b**. Also, in a moistened medium a deacetylated 1:1-adduct (**3b′**) was isolated instead of **3b**. The structure of **3b** was elucidated to be an endo [4+2]adduct by a direct comparison with the spectral data of **3a**; in the ^{1}H NMR spectrum, **3b** showed signals at δ 6.95—7.15, which were ascribable to H-13 and H-14, being lower than the corresponding signals of **3a**. This low-field shift indicated an intact ethoxycarbonyl group at C-11. The exo [4+2]adduct structure for **8** was deduced from the coupling constant (5.9 Hz) between H-1 and H-2 in the ^{1}H NMR spectrum.

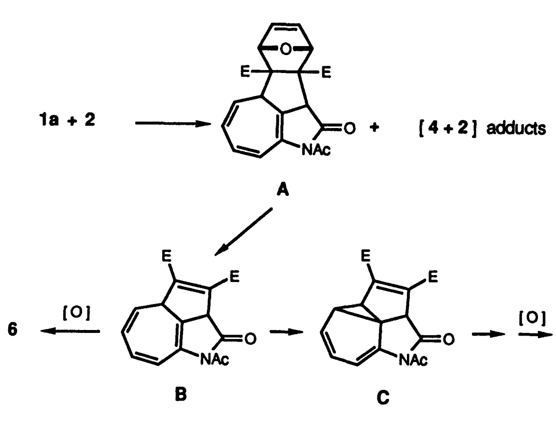
The reaction between 1-acetyl-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (**1c**) and **2** in anhydrous dioxane under 3000 bar afforded two products (**3c** and **3c′**) and a deacetyl derivative (**1c′**)[8] of **1c**. The latter adduct **3c′** was a deacetylated derivative of **3c**.

Photorearrangement of 7. The irradiation of **7** with a high-pressure mercury lamp (1 kW) gave three products (**9**—**11**). The structures of these products were similar to those obtained from the photolysis of 2-oxatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one derivatives (**12**).[9] Interestingly, a dihydroindenone (**11**) was isolated as a proto-photoisomer from **7** in this case; a similar photolysis of **12** gave an aromatized indan derivative (**13**).

Reaction Modes of 1 and 2. There was observed nearly equal amounts of two types of products in the cycloaddition reaction between **1** and **2**, as shown in Table 1. The product distributions were not similar to those of the reactions of **1** and DMBD in a refluxing acetonitrile.[5] For example, the reaction of cyclohepta[*b*]pyrrol-2(1*H*)-one (**1d**) and DMBD gave two ene



Scheme 2.



Scheme 3.

products in 51% and the deacetyl derivative of **5** in 35% together with a deacetyl derivative of **6** in 5% yields. The reaction of **1d** and **2** did not proceed even at 120 °C under 3000 bar, and the product distributions in the reactions of **1d** with DMBD and **1a** and **2** were completely different. Therefore, products **5** and **6** were formed via a 1:1-adduct (**A**) of **1a** and **2** and not formed from **1a** and DMBD, although DMBD could be available by a cycloreversion of **2** under the reaction conditions. An elimination of furan from **A** and a subsequent autooxidation, via **B**, should yield **6**. A valence bond isomerization of the cycloheptatriene function in **B** followed by a dehydrogenation should afford **5**. Thus, the [8+2]addition occurred exclusively

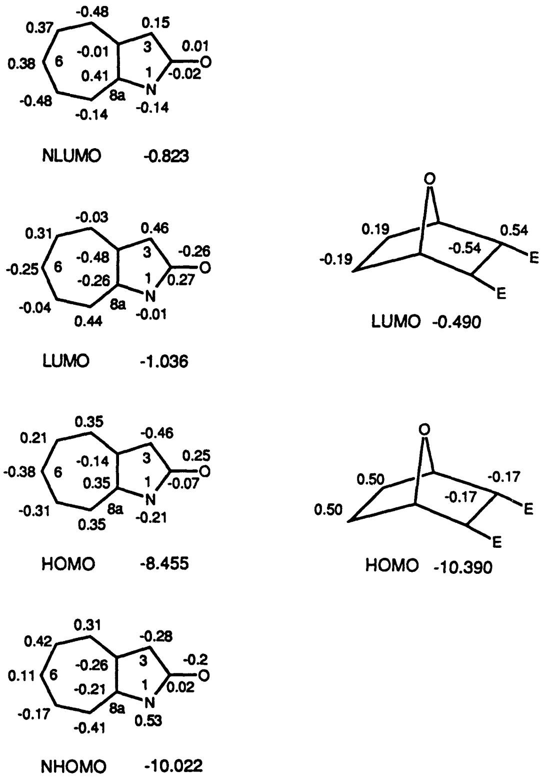


Fig. 1. Coefficients and energy levels of selected molecular orbitals of **1a** and **2**.

at positions of C-3 and C-4 in **1**. So far, no product reacted at C-3 and C-8a of **1** has been isolated, although the coefficient of C-4 in HOMO of **1a** was identical with that of C-8a from the MNDO calculation. An acetyl group might prevent an approach to the C-8a position of **2**. The reaction site of **2** in the [8+2]addition could be reasonably explained by the interaction of HOMO(**1a**) and LUMO(**2**), which favored a reaction to occur at the double bond with methoxycarbonyl groups.

Among [4+2]adducts identified, a new type of an adduct, **4**, should be worthy of note. This type of the product has never been isolated from reactions between cyclohepta[*b*]furan-2(2*H*)-ones and **2**.[3] Therefore, the formation of **4** might be explained in terms of the steric effect of an acetyl group on the nitrogen atom, which prevents an approach of **2** to the C-8a position of **1a**. The interactions of both LUMO(**1a**)-HOMO(**2**) and the NLUMO(**1a**)-HOMO(**2**) favored a [4+2]addition at a double bond having no substituents of **2**.[10]

Experimental

Elemental analyses were performed by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured by a JEOL GSX 270 H Model spectrometer in a $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in δ unit. Apparent coupling constants were obtained from the first-order analyses. Mass spectra were measured with a JEOL OlSG-2 spectrometer. IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer.

Cycloaddition of 1a and 2. a) A chlorobenzene solution (3 cm^3) of **1a** (191 mg) and **2** (293 mg) was heated at 120 °C for 20 h under 3000 bar. The solvent was removed under reduced pressure and the residue was chromatographed on a silica-gel column to give 45 mg (12%) of **3a**, 15 mg (4%) of **4**, 26.6 mg (8%) of **5**, 20 mg (6%) of **6**, and recovered **1a** (12.4 mg) and **2** (20 mg).

3a: colorless crystals, mp 202—203 °C; ^{1}H NMR δ=2.26 (1H, dd, J=8.1, 1.1 Hz), 2.56 (1H, d, J=8.1 Hz), 2.67 (3H, s), 3.43 (1H, dd, J=8.4, 8.1 Hz), 3.77 (3H, s), 3.81 (3H, s), 4.93 (1H, d, J=1.1 Hz), 5.69 (1H, d, J=1.1 Hz), 5.72 (1H, s), 6.21 (1H, d, J=10.3 Hz), 6.25 (1H, t, J=8.1 Hz), 6.30 (1H, dt, J=8.1, 1.1 Hz), and 6.72 (1H, dd, J=10.3, 8.4 Hz); ^{13}C NMR δ=26.6, 38.8, 46.2, 51.4, 52.4 (2C), 71.8, 83.7, 85.8, 117.3, 122.3, 128.8, 129.5, 144.5, 144.7, 146.4, 160.3, 162.7, 162.9, 170.8, and 171.6; IR 3010, 2890, 1740, 1705, 1640, and 1610 cm^{-1}; UV (MeOH) 245.6 (ε 9600) and 282.8 nm (7300).

Found: C, 63.67; H, 4.84; N, 3.54%. Calcd for $C_{21}H_{19}NO_7$: C, 63.46; H, 4.82; N, 3.52%.

4: colorless crystals, mp 202 °C; ^{1}H NMR δ=2.39 (1H, d, J=8.1 Hz), 2.55 (3H, s), 2.70 (1H, d, J=8.1 Hz), 3.52 (1H, dd, J=9.5, 8.1 Hz), 3.81 (6H, s), 3.89 (1H, d, J=7.0 Hz), 4.93 (1H, s), 5.06 (1H, s), 5.87 (1H, d, J=1.8 Hz), 6.14 (1H, dd, J=8.4, 7.0 Hz), 6.45 (1H, dd, J=8.4, 8.1 Hz), and 7.69 (1H, dd, J=9.5, 1.8 Hz); ^{13}C NMR δ=26.6, 37.8, 41.0, 44.4, 47.9, 52.4 (2C), 86.0, 86.2, 115.5, 127.2, 127.4, 136.6, 138.0, 144.7, 145.7, 154.4, 162.7 (2C), 168.4, and 171.1; IR 2890, 1710, 1630, 1595, and 1430 cm^{-1}; UV (MeOH) 246.4 (ε 11700), 285.4 (9100), and 421.4 nm (500).

Found: C, 63.55; H, 4.83; N, 3.47%. Calcd for $C_{21}H_{19}NO_7$: C, 63.46; H, 4.82; N, 3.52%.

5: yellow prisms, mp 172—173 °C (lit,[5] mp 174—176 °C).

6: reddish crystals, mp 183—185 °C; ^{1}H NMR δ=2.82 (3H, s), 3.97 (3H, s), 4.07 (3H, s), 7.91 (1H, dd, J=10.3, 9.5 Hz), 8.26 (1H, t, J=10.3 Hz), 9.06 (1H, d, J=10.3 Hz), and 9.36 (1H, d, J=9.5 Hz); ^{13}C NMR δ=26.5, 52.1, 53.0, 113.7, 120.9, 122.1, 131.4, 137.3, 137.5, 139.2, 142.7, 143.1, 147.2, 161.0, 164.1, 165.3, and 172.4; IR 2880, 1740, 1695, and 1595 cm^{-1}; UV (MeOH) 232.4 (ε 21600), 257.6 (42300), 283.2 (26300), and 367.4 nm (9500).

Found: C, 62.32; H, 3.98; N, 4.05%. Calcd for $C_{17}H_{13}NO_6$: C, 62.39; H, 4.00; N, 4.28%.

b) A chlorobenzene solution (1 cm^3) of **1a** (130 mg) and **2** (350 mg) was heated at 130 °C for 20 h in a sealed tube under a nitrogen atmosphere. After removing the solvent, the residue was chromatographed on a silica-gel column to give 35.8 mg (16%) of **5**, 18 mg (13%) of **7**, and recovered **1a** (52.2 mg) and **2** (106 mg).

7: colorless crystals, mp 136—138 °C; ^{1}H NMR δ=2.63 (3H, s), 3.90 (1H, dtm, J=8.1, 7.7 Hz), 5.73 (1H, s), 5.90 (1H, d, J=10.3 Hz), 6.28 (2H, dd, J=7.7, 1.5 Hz), 6.54 (2H, t, J=7.7 Hz), and 6.57 (1H, dd, J=10.3, 8.1 Hz); ^{13}C NMR δ=25.2, 39.5, 70.5, 118.0, 119.6, 131.5 (2C), 133.1 (2C), 140.2, 153.2, 169.7, and 170.3; IR 2905, 1730, 1620, and 1380 cm^{-1}; UV (MeOH) 260.6 nm (ε 9300).

Found: C, 73.28; H, 5.22; N, 6.58%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

Cycloaddition of 1b and 2. a) An anhydrous dioxane solution (2.5 cm^3) of **1b** (54 mg) and **2** (100 mg) was heated at 120 °C under 3000 bar for 20 h. Silica-gel chromatography of the residue gave 16 mg (26%) of **3b**, 4 mg (6.5%) of **8**, and recovered **2** (50 mg) and **1b′** (16 mg).

3b: colorless crystals, mp 125—126 °C; ^{1}H NMR δ=1.38 (3H, t, *J*=7.3 Hz), 2.27 (1H, d, *J*=7.7 Hz), 2.59 (1H, dd, *J*=7.7, 1.1 Hz), 2.71 (3H, s), 3.53 (1H, m), 3.78 (3H, s), 3.81 (3H, s), 4.37 (2H, q, *J*=7.3 Hz), 4.94 (1H, d, *J*=1.1 Hz), 5.64 (1H, d, *J*=1.1 Hz), 6.3 (2H, m), and 6.95—7.15 (2H, m); ^{13}C NMR δ=14.2, 27.0, 39.5, 46.4, 51.7, 52.5 (2C), 61.6, 70.6, 83.8, 85.7, 117.3, 121.2, 128.8, 130.4, 144.5, 146.8, 149.7, 161.8, 162.4, 162.7, 162.8, 166.8, and 171.8; IR 3000, 1740, 1640, 1610, and 1580 cm^{-1}; UV (MeOH) 248.2 (ε 11100) and 296.4 nm (11700).

Found: C, 61.48; H, 4.96; N, 3.05%. Calcd for $C_{24}H_{23}NO_9$: C, 61.40; H, 4.94; N, 2.98%.

8: colorless crystals, mp 172—173 °C; ^{1}H NMR δ=1.39 (3H, t, *J*=7.3 Hz), 2.65 (1H, dd, *J*=8.8, 5.9 Hz), 2.69 (3H, s), 3.7 (1H, m), 3.73 (1H, d, *J*=8.8 Hz), 3.75 (3H, s), 3.81 (3H, s), 4.37 (2H, q, *J*=7.3 Hz), 4.61 (1H, s), 4.89 (1H, d, *J*=1.1 Hz), 6.18 (1H, d, *J*=8.4 Hz), 6.42 (1H, dd, *J*=8.4, 7.3 Hz), 6.69 (1H, dd, *J*=10.6, 8.4 Hz), and 7.31 (1H, d, *J*=10.6 Hz); ^{13}C NMR δ=14.3, 26.2, 38.1, 42.8, 48.5, 52.4, 52.5, 61.5, 70.4, 79.9, 83.8, 118.6, 125.9 (2C), 133.2, 134.4, 143.9, 145.6, 161.5, 161.7, 161.8, 162.6, 166.4, and 170.4; IR 3000, 2950, and 1720 cm^{-1}; UV (MeOH) 243.8 (ε 10000) and 299.4 nm (10300).

Found: C, 61.19; H, 4.94; N, 2.99%. Calcd for $C_{24}H_{23}NO_9$: C, 61.40; H, 4.94; N, 2.98%.

1b′: mp 185—188 °C (lit,[7] mp 189—190 °C).

b) A dioxane solution (2 cm^3) of **1b** (80 mg) and **2** (240 mg) was heated at 115 °C for 20 h under 3000 bar. Silica-gel chromatography of the mixture gave 35 mg (45%) of **3b′**, 26 mg of **1b′**, and recovered **2** (125 mg).

3b′: colorless crystals, mp 197—198 °C; ^{1}H NMR δ=1.34 (3H, t, *J*=7.0 Hz), 2.27 (1H, d, *J*=8.1 Hz), 2.50 (1H, d, *J*=8.1 Hz), 3.52 (1H, dd, *J*=8.4, 7.7 Hz), 3.72 (3H, s), 3.81 (3H, s), 4.33 (2H, q, *J*=7.0 Hz), 4.95 (1H, s), 5.45 (1H, s), 6.00 (1H, d, *J*=8.8 Hz), 6.29 (1H, dd, *J*=8.8, 7.7 Hz), 6.78 (1H, dd, *J*=10.6, 8.4 Hz), 7.06 (1H, d, *J*=10.6 Hz), and 8.63 (1H, br s); ^{13}C NMR δ=14.2, 39.5, 43.5, 49.8, 52.4, 52.5, 61.1, 65.8, 84.3, 85.5, 118.4, 121.9, 130.6, 132.0, 145.0, 145.4 (2C), 162.1, 162.3, 162.5, 162.6, and 169.9; IR 3400, 3200, 3100, 1740, 1640, and 1570 cm^{-1}; UV (MeOH) 248.6 (ε 10150) and 285.8 nm (11400).

Found: C, 61.46; H, 4.78; N, 3.26%. Calcd for $C_{22}H_{21}NO_8$: C, 61.82; H, 4.95; N, 3.28%.

Cycloaddition of 1c and 2. An anhydrous dioxane solution (1 cm^3) of **1c** (50 mg) and **2** (120 mg) was heated at 120 °C under 3000 bar for 20 h. Silica-gel chromatography of the mixture gave 4 mg (20%) of **3c**, 4.5 mg (24%) of **3c′**, and **1c′** (30 mg).

3c: colorless crystals, mp 198 °C (decomp); ^{1}H NMR δ=2.28 (1H, d, *J*=8.1 Hz), 2.59 (1H, dd, *J*=8.1, 1.1 Hz), 2.70 (3H, s), 3.6 (1H, m), 3.79 (3H, s), 3.81, (3H, s), 4.95 (1H, d, *J*=1.4 Hz), 5.64 (1H, s), 6.32 (2H, m), 6.53 (1H, d, *J*=10.3 Hz), and 7.14 (1H, dd, *J*=10.3, 8.8 Hz); ^{13}C NMR δ=26.7, 39.9, 46.6 (2C), 51.9, 52.6, 72.2, 83.7, 85.8, 102.6, 110.6, 120.7, 127.9, 130.8, 144.3, 146.7, 152.2, 162.4, 162.6, 165.4, 166.9, and 171.3; IR 2975, 2240, 1720, and 1620 cm^{-1}; UV (MeOH) 243.8 (ε 5700) and 300.8 nm (6300).

Found: *m/z* 380.1015 ($M^+ - CH_3CO$). Calcd for $C_{20}H_{15}N_2O_6$: 380.1008.

3c′: colorless crystals, mp 201—203 °C; ^{1}H NMR δ=2.27 (1H, d, *J*=8.1 Hz), 2.55 (1H, d, *J*=8.1 Hz), 3.60 (1H, t, *J*=8.8 Hz), 3.79 (3H, s), 3.83 (3H, s), 4.95 (1H, d, *J*=1.5 Hz), 5.26 (1H, s), 5.99 (1H, d, *J*=8.8 Hz), 6.33 (1H, t, *J*=8.8 Hz), 6.55 (1H, d, *J*=10.6 Hz), 6.93 (1H, dd, *J*=10.6, 8.8 Hz), and 7.76 (1H, br s); ^{13}C NMR (DMSO-d_6) δ=42.8, 49.2, 52.2, 52.3, 67.0, 78.9, 82.8, 84.8, 101.5, 112.4, 119.8, 129.4, 132.5, 143.1, 146.6, 149.3, 161.9, 162.6, 166.4, and 166.6; IR 3400, 2975, 2240, 1710, 1640, and 1620 cm^{-1}; UV (MeOH) 285.4 (ε 13000) and 423.4 nm (1300).

Found: C, 62.14; H, 4.05; N, 7.03%. Calcd for $C_{20}H_{16}N_2O_6 \cdot 1/3H_2O$: C, 62.18; H, 4.31; N, 7.25%.

1c′: mp>280 °C (lit,[8] mp 305 °C (decomp)).

Cycloaddition of 1d and 2. A chlorobenzene solution (1 cm^3) of **1d** (72 mg) and **2** (138 mg) was heated at 120 °C under 3000 bar for 20 h. Silica-gel chromatography of the mixture gave only **1d**.

Cycloreversion of 3a. A xylene solution (1 cm^3) of **3a** (55 mg) was heated at 140 °C for 20 h in a sealed tube. The mixture was chromatographed on a silica-gel column to give 12 mg (56%) of **7**, 11 mg (60%) of 3,4-bis(methoxycarbonyl)furan, and recovered **3a** (15 mg).

Photolysis of 7. A $CHCl_3$ solution (1 cm^3) of **7** (30 mg) was irradiated by a high-pressure mercury lamp (1 kW) for 3 h. The mixture was chromatographed on a silica-gel column to give 4.7 mg (19%) of **9**, 4.5 mg (18%) of **10**, and 3.8 mg (15%) of **11**.

9: colorless crystals, mp 130 °C; ^{1}H NMR δ=2.58 (3H, s), 2.77 (2H, m), 3.13 (1H, t, *J*=7.0 Hz), 5.65—5.75 (2H, m), 5.71 (1H, s), and 6.37 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=21.6, 25.3, 30.3 (2C), 67.2, 112.8, 119.2 (2C), 129.3 (2C), 162.9, 169.7, and 169.9; IR 3000, 1720, and 1650 cm^{-1}; UV (MeOH) 222.2 (ε 15900) and 268.4 nm (3850).

Found: C, 72.88; H, 5.10; N, 6.43%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

10: colorless crystals, mp 129—131 °C; ^{1}H NMR δ=2.10 (1H, td, *J*=7.7, 4.8 Hz), 2.55 (3H, s), 2.76 (1H, dd, *J*=7.7, 6.2 Hz), 2.95 (1H, ddd, *J*=7.7, 6.2, 2.2 Hz), 5.18 (1H, d, *J*=5.1 Hz), 5.69 (1H, s), 5.96 (1H, dd, *J*=5.1, 2.2 Hz), 6.12 (1H, dd, *J*=9.9, 4.8 Hz), and 6.59 (1H, d, *J*=9.9 Hz); ^{13}C NMR δ=25.5, 26.6, 37.0, 42.0, 74.2, 114.7, 122.4, 131.9, 133.4, 134.0, 161.4, 169.7, and 170.2; IR 3000, 1720, and 1625 cm^{-1}; UV (MeOH) 238.0 (ε 9800) and 302.6 nm (5900).

Found: C, 73.28; H, 4.94; N, 6.58%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

11: colorless crystals, mp 123 °C; ^{1}H NMR δ=2.64 (3H, s), 3.56 (1H, dm, *J*=12.1 Hz), 4.0—4.2 (1H, m), 5.51 (1H, dd, *J*=9.5, 4.0 Hz), 5.71 (1H, dd, *J*=2.9, 2.6 Hz), 5.79 (1H, dd, *J*=6.2, 1.8 Hz), 5.88 (1H, ddd, *J*=9.5, 6.2, 2.6 Hz), 6.61 (1H, dd, *J*=5.5, 2.6 Hz), and 6.77 (1H, dd, *J*=5.5, 2.9 Hz); ^{13}C NMR δ=28.0, 40.3, 46.2, 110.2, 114.8, 121.9, 122.5, 129.8, 132.7, 152.1, 166.1, 167.8, and 172.3; IR 3010 and 1695 cm^{-1}; UV (MeOH) 265.8 nm (ε 19100).

Found: C, 73.05; H, 5.07; N, 6.49%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

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