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High-Pressure Cycloaddition Reaction of Tropone with Furans

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Thermal reactions of tropone with furan and 2-methoxyfuran mainly gave the endo-[4+2] cycloadducts, the kinetically controlled products, at 3000 bar. In the latter case, the product further reacted with tropone to yield 2 : 1-adducts. On the other hand, the reaction with 3,4-dimethoxyfuran under similar conditions yielded mainly the exo-[4+2] adducts, the thermodynamically controlled products. The predominant formation of the endo-Diels–Alder adducts with furans under the high-pressure conditions may be valuable from a synthetic point of view.

We have recently reported the high-pressure kinetic analysis of the electrocyclic reactions of tropone (**1**) to show the normal volume profiles for the cycloadditions of **1**.[1,2] Accordingly, the ordinary pressure effect should apply to **1**, and under the high-pressure conditions, even the hitherto unsuccessful Diels–Alder reaction of **1** with furans, due to a facile cycloreversion, may occur.[3] Here, we describe the reaction of **1** with furan (**2**), 2-methoxyfuran (**3**), and 3,4-dimethoxyfuran (**4**).

Results and Discussion

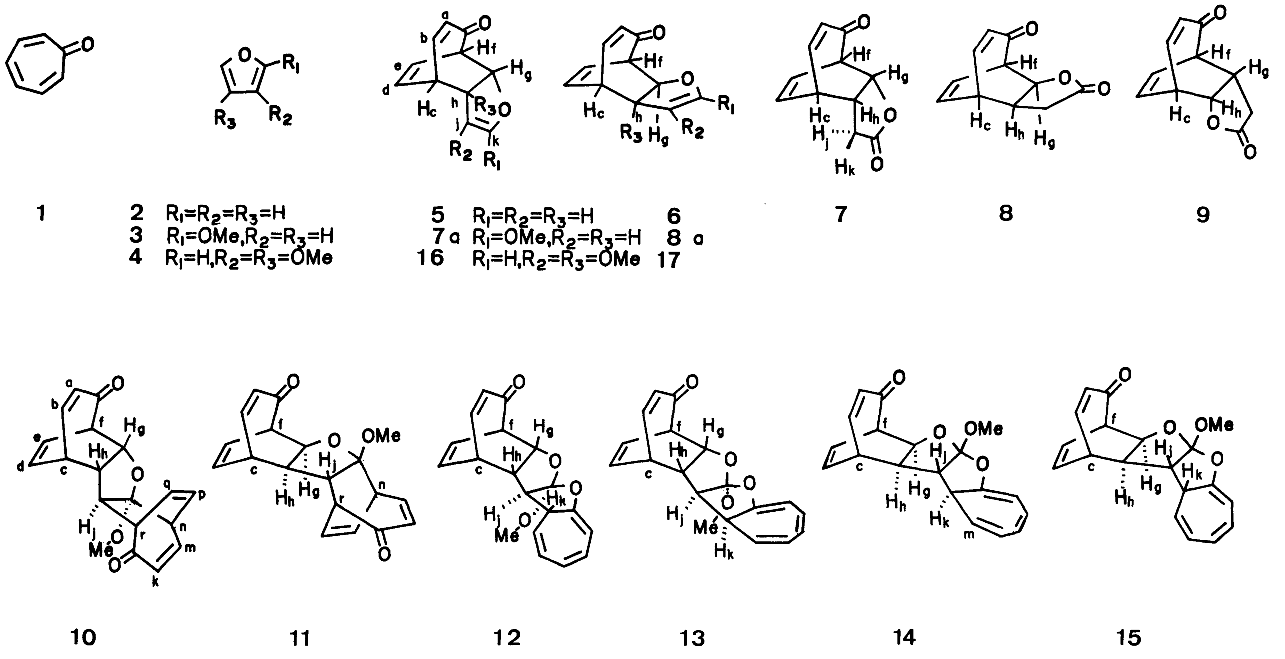
Thermal Cycloaddition of 1 with Furans. Heating of an isopropylbenzene (IB) solution of **1** and **2** in a Teflon ampule placed in a pressure vessel (3000 bar)[4] at 130 °C for 10 h yielded, after silica-gel column chromatography, two 1:1-adducts (**5** and **6**). A similar treatment of **1** and **3** yielded three 1 : 1-adducts **7**—**9**, together with six 2 : 1-adducts **10**—**15**, which were derived from further cycloaddition of **1** to **7a** or **8a**, proto-adducts leading to **7** or **8**. With **4**, **1** afforded two 1 : 1-adducts **16** and **17** in 8 and 28% yields, respectively. The results are summarized in Table 1.

In comparison with these high-pressure cycloadditions, the reaction of **1** under ordinary pressure yielded inferior results; heating **1** and **2** in a sealed tube at 130 °C caused no reaction, while under similar conditions, **1** and **3** yielded only **7** and **8**, and **1** and **4** yielded a mixture of products too complicated to permit further investigation.

Table 1. High-Pressure Cycloaddition Reactions of Tropone with Furans

Yield/%	endo-[4+2]	exo-[4+2]	endo/exo
1+2	6 (0)[a)]	5 (0)	1.2 (—)
1+3	35 (13) 45[b)]	13 (3) 18[b)]	2.7 (4.3)
1+4	8 (0.5)	28 (0.5)	0.29 (1)

a) Figures in parenthesis are yields at room temperature.
b) These values are yields including 2 : 1-cycloadducts.



Scheme 1.

Table 2. Selected NMDR Data of **10**

Irradiated frequency at	Behavior of singnal ascribable to										
	H_j	H_h	H_c	H_r	H_f	H_n	H_g	H_a	H_k	H_m	H_b
2.46(H_j)		—a)	×b)	○c)	×	×	×	×	×	×	×
2.67(H_h)	—		$J=2$d)	×	×	×	$J=8.5$	×	×	×	×
3.2 (H_c)	×	$J=2$		—	—	—	×	$J=0.5$	×	×	$J=8.5$
3.4 (H_r)	○	×	—		—	—	×	×	$J=2$	×	×
3.58(H_f)	×	×	—	—		—	$J=1.5$	$J=2$	×	×	×
3.66(H_n)	×	×	—	—	—		×	×	$J=1$	$J=8.5$	×
4.74(H_g)	×	$J=8.5$	×	×	$J=1.5$	×		×	×	×	×
5.62(H_a)	×	×	$J=0.5$	×	$J=2$	×	×		×	×	$J=11$
5.76(H_k)	×	×	×	$J=2$	×	$J=1$	×	×		$J=11$	×
6.84(H_m)	×	×	×	×	×	$J=8.5$	×	×	$J=11$		—
7.02(H_b)	×	×	$J=8.5$	×	×	×	×	$J=11$	×	—	

a) Not observable. b) No change in signal shape. c) Appreciable sharpening occurred. d) Figures indicate the confirmed coupling values by NMDR.

Structures of 1 : 1-Adducts. The 1 : 1-adducts from **3** (**7**—**9**) exhibited no methoxyl signals in the ^{1}H NMR spectra to indicate a hydrolytic removal of the methoxyl group under the chromatographic conditions to form γ-lactone functions. Other structural features were parallel with the other adducts from **2** and **4**. The structures of these 1 : 1-adducts were clarified by mutual comparisons of the ^{1}H NMR analysis.5) Namely, the ^{1}H NMR spectra6) of all 1 : 1-adducts revealed signals of the α,β-unsaturated keto groups at $\delta=6.8$—7.1 and 5.8—6.2 with the coupling constant of ca. 11 Hz, and the latter signals long-range-coupled with the bridge-head methine protons, being characteristic for the [4+2] adducts from **1**.5) In addition, the ^{1}H NMR of **5**, **7**, and **16** exhibited the smaller J_{fg} (2.5 Hz for **5** and 2 Hz for **7** and **16**), while those of **6**, **8**, and **17** did larger J_{fg} (7 Hz for **6**, 7.5 Hz for **8**, and 6.5 Hz for **17**). Therefore, endo-[4+2]7) structures could be assigned for the formers and exo-[4+2] ones for the latter.8)

The remaining **9** was another endo-[4+2] cycloadducts; its spin-spin splitting patterns ($J_{gh}=7.5$ and $J_{ch}=2$ Hz) ascribable to the lactonic proton indicated to be a regioisomer of **7**.

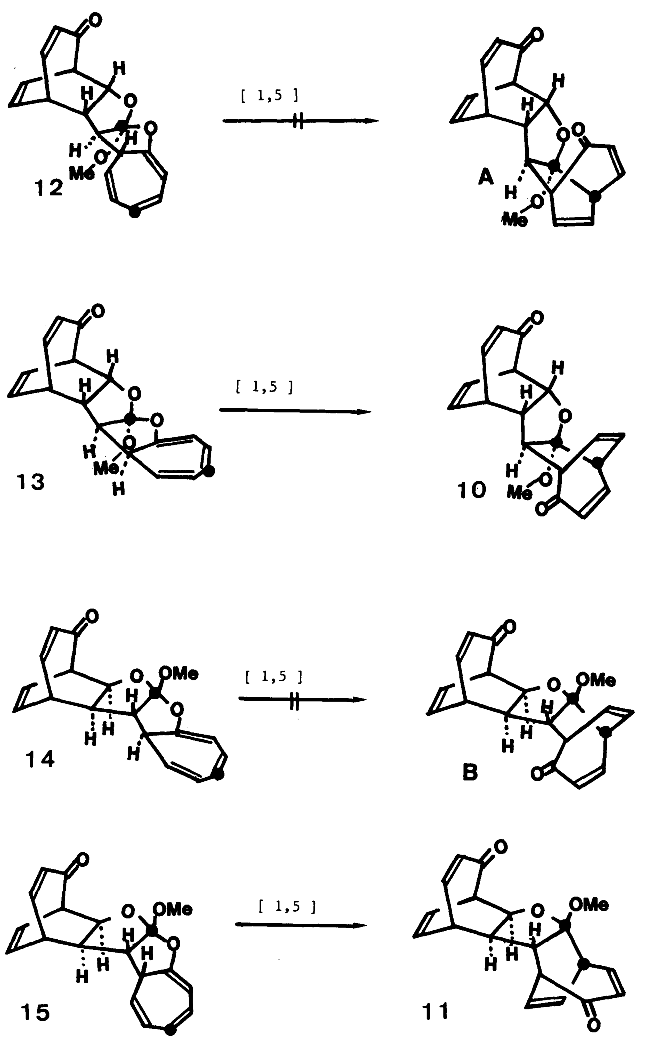
Structures of 2 : 1-Adducts. Structures of 2 : 1-adducts from **1** and **3** were determined by detailed 400 MHz-decoupled NMR analysis (NMDR) or measurements of the nuclear Overhauser effect (NOE). The **10** and **11**, having two carbonyl carbon signals in the ^{13}C NMR spectra, were [4+2]-[4+2] cycloadducts. The ^{1}H NMR spectra of **10** and **11** revealed $J_{gh}=8.5$, $J_{fg}=1.5$, and $J_{jr}=0$ Hz for **10** and $J_{gh}=8.5$, $J_{fg}=6.5$, and $J_{jr}=0$ Hz for **11**, and clarified their structures to be endo-[4+2]-endo-[4+2] and exo-[4+2]-endo-[4+2] cycloadducts, respectively. The regiochemistry of the second addition step to tropone was confirmed by NMDR; irradiation of the bridge-head protons (H_r) of **10** and **11** changed the broad doublet of H_j to sharp doublets, respectively. While, H_n of **10** and **11**, spin-coupled with the β-protons (H_m) of α,β-unsaturated keto group, was irradiated, the splitting patterns of H_j did not change at all. Hence, H_j and H_r of **10** and **11** are mutually coupled and their structures are unambiguously clarified as was shown in Scheme 1. The changes in shape of the signals caused by intensive NMDR experiments are tabulated in Tables 2 and 3.

Table 3. Selected NMDR Data of **11**

Irradiated frequency at	Behaviors of signal ascribable to						
	H_h	H_j	H_c	H_r	H_n	H_f	H_g
2.4 (H_h)		—a)	×b)	×	×	×	$J=8.5$c)
2.58 (H_j)	—		×	○	×	×	○d)
3.4 (H_c)	×	×		—	×	—	×
3.43 (H_r)	×	○	—		○	○	×
3.75 (H_n)	×	×	—	○		—	○
3.87 (H_f)	×	×	—	○	—		$J=6.5$
4.65 (H_g)	$J=8.5$	○	×	×	○	$J=6.5$	

a) Not observable. b) No change in signal shape. c) Figures indicate the confirmed coupling values by NMDR. d) Appreciable sharpening occurred.

On the other hand, **12**—**15** each revealed only one carbonyl carbon ^{13}C NMR spectrum; one of the tropone molecules had thus reacted as the 8π-cycloaddend. Therefore, they are [4+2]-[8+2] cycloadducts. The observed coupling sequences of the methine protons clarified the stereochemistry, and particularly for analyses of [8+2] adducts, there are good model compounds already investigated;9,10) e.g., **12** [$J_{fg}=2$, $J_{gh}=8.5$, $J_{jk}=0$, $J_{hj}=7$, and $J_{ch}=2$ Hz] and **13** [$J_{fg}=2$, $J_{gh}=8.5$, $J_{jk}=7.5$, and $J_{hj}=7.5$ Hz] are derived from **7a**, while **14** [$J_{fg}=7$, $J_{gh}=8.5$, $J_{jk}=1$, and $J_{hj}=5$ Hz] and **15** [$J_{fg}=7$, $J_{gh}=8.5$, $J_{jk}=7.5$, $J_{hj}=6$, and $J_{ch}=5$ Hz] are from **8a**. The assignments were supported by NOE observations; i.e., an irradiation with the frequency of H_h-signal of **12** enhanced its H_g- and H_k-signals, and similar irradiations with the frequencies of H_h- and H_j-signals of **14** enhanced the H_g- and H_m-signals. When the isomeric **12**—**15** were separately heated in a sealed NMR tube respectively, although the isolated yields were not sufficiently high due to the instability towards air, stereospecific formation of **10** from **13** and **11** from **15** was confirmed and the identities with

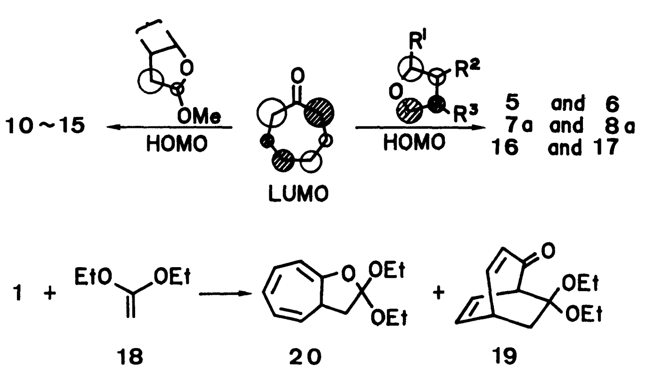


Scheme 2.

authentic **10** and **11** were established by the ^{1}H NMR spectral comparison. Moreover, the stereospecific isomerization without formation of fragmented 1 : 1-adducts eliminated the dissociation-recombination process. Therefore, considering these structural relationships, **13** and **15** were deduced to have endo-[4+2]-cis-[8+2] and exo-[4+2]-cis-[8+2] structures,[11] respectively.

Mechanism of the Cycloaddition. As shown in Table 1, furans only gave [4+2] cycloadducts with **1**, being parallel to cyclopentadiene at 145 °C,[8] but not to 2,5-dimethyl-3,4-diphenylcyclopentadienone, which gave a [4+2] cycloadduct above 100 °C and predominantly a [6+4] cycloadduct at 60 °C.[12] Among 1 : 1-adducts of **1** with furans, there was no [2+4] or [6+4] cycloadduct formed at all, and a predominant occurrence of the endo-[4+2] cycloadducts is noteworthy. In parallel to the previous study of 3,4-dialkoxyfuran with alkyl coumalates,[13] **4** reacted solely as the 2π-component, a dienophile, throughout.

The regioselectivities of these reactions can be explained by consideration of the LUMO(**1**)-HOMO(furans) interactions, where the largest coefficients are at the C-2(7) positions of **1**, the C-2 positions of **2** and **4**, and the C-5 position of **3**.[14]



Scheme 3.

The reaction of **1** with **3** yielded six 2 : 1-adducts. The second step of tropone incorporation occurred at a dialkoxyethene part of **7a** and **8a** in two different fashions with a high regioselectivity; one is a [4+2] adduct and the other an [8+2] ([8+2]/[4+2]=3.4).[15]

The predominant formation of [8+2] adducts is parallel to the previous result of the reaction of **1** with 1,1-diethoxyethene(**18**).[10] The high regioselectivity in the second step could be reasonably explained by Frontier Orbital interactions.[16] The energies of the HOMO of the dialkoxyethene part in **7a** and **8a** are estimated to be around −7.5 eV, and those of the LUMO around −4.5 eV.[14] Therefore, considering Frontier Orbitals of **1**,[17] the LUMO(**1**)-HOMO(**7a** and **8a**) interactions[16] are primarily important to 2 : 1-adducts formation. However, these could not explain the periselectivity of the second step of cycloaddition; i.e., the LUMO of **1** has the largest coefficient at the C-2 and the next at the C-5, and the coefficient of the carbonyl oxygen is null.[17] Furthermore, the regiochemistry of the second step of the [4+2]-[4+2] addition is opposite to that of the reported [4+2] adduct (**19**) from **1** and **18**.[10,18] Therefore, the [4+2]-[8+2] adducts may be the thermodynamically stable products accumulated by mutual isomerization with the [4+2]-[4+2] adducts via a [1,5] bond migration. As has been stated, **13** and **15** indeed rearranged to **10** and **11**. A failure to isolate the corresponding [4+2]-[4+2] products (**A** and **B**) from **12** or **14**, however, did not contradict but supported the results of the reaction of **1** with **3**. Since the isomerization occurred only with the stereomers having the cis-geometry, the difference in the thermodynamic stability should be critical; as the molecular model suggests, both **12** and **14** possess the stable trans-trans-geometry for H_h-H_j-H_k and as a result, the equilibria could not produce detectable amounts of **A** and **B** while heating.

In addition, although a stepwise rearrangement was unlikely on the basis of the observed stereospecificity, the mechanism should be analyzed carefully. If the [1,5] sigmatropy is operative in this particular case, the trans-cis system present in the reactive diene site of the molecule forces the migrating group to flight for long distance,[19] but, the doubly-allylic methine hydrogen was inert against the Woodward-Hoffmann rule-allowed [1,5] sigmatropy. At present, due to the instability of our [8+2] adducts,[20] no further study is possible.

Furthermore, the endo/exo ratio is dependent on the substituents on furans, and under higher pressures, the amount of the exo-isomer which is the thermodynamically controlled product increased in the reaction of **1** with **4**.

Finally, although the present pressure, 3000 bar, being a limit of our apparatus, is not high enough in a preparative point of view, yet, the observed pressure effect was significant, and under higher pressures, the yields and the endo/exo-selectivity of the reaction can be improved.[21,22]

Experimental

Elemental analyses were performed by Miss S. Hirashima, of the Research Institute of Industrial Science, Kyushu University. The NMR spectra were recorded either on a JEOL GX 400 Model or on a JEOL FX 100 Model Spectrometer in $CDCl_3$ solution; the chemical shifts were expressed in δ units. The IR spectra were taken in KBr disks or in $CHCl_3$ solution using a Jasco IR-A 102 Spectrometer. The mass spectra were measured on a JEOL OlSG-2 Spectrometer. The UV spectra were measured by means of a Hitachi U-3200 Spectrophotometer.

Diels-Alder Reaction of 1 with 2. **a)** An IB solution (3 cm^3) of **1** (103 mg) and **2** (672 mg) was heated at 130 °C for 10 h in a Teflon ampule under 3000 bar. After cooling to room temperature, the mixture was decompressed and chromatographed on a silica-gel column to give unreacted **1** [61.9 mg; 60%] and the mixture of adducts, which was purified via high-pressure liquid chromatography (HPLC; Micropolasil with hexane-AcOEt) to give **5** [a colorless oil, 4.2 mg; 6%. Found: *m/z*, 174.0682 (M^+). Calcd for $C_{11}H_{10}O_2$: M, 174.0682. ^{1}H NMR δ=3.28 (H_c,[6] tdm, J=8.5, 2.5 Hz), 3.67 (H_h, dtd, J=10, 2.5, 2 Hz), 3.95 (H_f, dm, J=7 Hz), 4.70 (H_j, td, J=2.5, 1 Hz), 5.00 (H_g, ddd, J=10, 2.5, 1 Hz), 5.72 (H_a, ddd, J=11, 2, 1 Hz), 6.07 (H_e, ddt, J=8.5, 7, 1 Hz), 6.27 (H_k, dd, J=2.5, 2 Hz), 6.40 (H_d, tm, J=8.5 Hz), and 7.10 (H_b, dd, J=11, 8.5 Hz). ^{13}C NMR δ=40.7, 50.4, 59.9, 81.5, 102.9, 125.2, 129.8, 136.7, 148.5, 154.2, and 194.4. IR ν 1670 cm^{-1}. UV λ_{max}^{MeOH} 209 nm (ε=7600)] and **6** [colorless needles, mp 70—72 °C, 3.1 mg; 5%. Found: *m/z*, 174.0681 (M^+). ^{1}H NMR δ=3.3—3.5 (H_c and H_h, m), 4.07 (H_f, tm, J=7 Hz), 4.82 (H_j, t, J=2.5 Hz), 5.11 (H_g, dd, J=11, 7 Hz), 5.88 (H_a, dd, J=11, 2 Hz), 5.99 (H_e, ddd, J=8.5, 7, 1 Hz), 6.29 (H_k, dd, J=2.5, 1.5 Hz), 6.53 (H_d, ddd, J=8.5, 7, 1 Hz), and 6.81 (H_b, dd, J=11, 9 Hz). ^{13}C NMR δ=40.9, 49.9, 56.7, 81.9, 102.2, 125.3, 131.6, 139.5, 148.2, 151.4, and 193.9. IR ν 1680 cm^{-1}. UV λ_{max}^{MeOH} 212 nm (ε=7400)].

b) An IB solution (1 cm^3) of **1** (44.4 mg) and **2** (307 mg) was heated at 130 °C for 10 h in a sealed tube. After removal of the volatile material, no compound was isolated other than the recovered **1**.

Diels-Alder Reaction of 1 with 3. **a)** An IB solution (51 cm^3) of **1** (768 mg) and **3** (6.93 g) was heated at 130 °C for 10 h under 3000 bar. Silica-gel column chromatography of the mixture afforded **7** [colorless needles, mp 138—140 °C, 474 mg; 35%. Found: C, 69.35; H, 5.33%; *m/z*, 190.0627 (M^+). Calcd for $C_{11}H_{10}O_3$: C, 69.45; H, 5.31%; M, 190.0629. ^{1}H NMR δ=2.28 (H_j, dd, J=18, 5 Hz), 2.88 (H_k, dd, J=18, 11 Hz), 3.26 (H_h, ddddd, J=11, 8, 5, 2, 1 Hz), 3.36 (H_c, ddm, J=8.5, 7 Hz), 3.90 (H_f, dtd, J=7, 2, 1 Hz), 5.04 (H_g, ddd, J=8, 2, 1 Hz), 5.78 (H_a, ddd, J=11, 2, 1 Hz), 6.18 (H_e, ddt, J=8.5, 7, 1 Hz), 6.60 (H_d, ddt, J=8.5, 7, 1 Hz), and 7.14 (H_b, dd, J=11, 8.5 Hz). ^{13}C NMR δ=34.7, 38.9, 39.9, 59.1, 79.7, 127.2, 130.4, 136.2, 152.7, 175.9, and 192.7. IR ν 1780 and 1670 cm^{-1}. UV λ_{max}^{MeOH} 228 nm (ε=7500)], **8** [colorless needles, mp 137—139 °C, 175 mg; 13%. Found: C, 69.39; H, 5.36%; *m/z*, 190.0628 (M^+). ^{1}H NMR δ=2.2—3.1 (H_h, H_j, and H_k, m), 3.46 (H_c, ddd, J=8.5, 7, 4 Hz), 4.10 (H_f, tdd, J=7.5, 2, 1 Hz), 5.04 (H_g, dd, J=8, 7.5 Hz), 5.94 (H_a, ddd, J=11, 2, 1 Hz), 6.04 (H_e, ddd, J=8.5, 7.5, 1 Hz), 6.64 (H_d, ddd, J=8.5, 7, 1 Hz), and 6.94 (H_b, dd, J=11, 8.5 Hz). ^{13}C NMR δ=32.6, 39.7, 40.4, 56.3, 78.5, 124.5, 133.5, 140.2, 148.6, 176.0, and 192.7. IR ν 1780 and 1670 cm^{-1}. UV λ_{max}^{MeOH} 227 nm (ε=7100)], and a mixture of adducts, from which, an HPLC fractionation gave **9** [colorless crystals, mp 103—105 °C, 20 mg; 1%. Found: *m/z*, 190.0631 (M^+). ^{1}H NMR δ=2.3 (H_g, br m), 2.8—3.2 (H_j and H_k, m), 3.46 (H_f, ddd, J=7.5, 2.5, 1.5 Hz), 3.76 (H_c, dddm, J=9, 7, 2 Hz), 5.02 (H_h, dd, J=7.5, 2 Hz), 5.88 (H_a, ddd, J=11, 2, 1 Hz), 6.22 (H_e, ddt, J=8.5, 7.5, 1 Hz), 6.50 (H_d, ddt, J=8.5, 7, 1 Hz), and 6.98 (H_b, dd, J=11, 9 Hz). ^{13}C NMR δ=34.1, 35.1, 41.4, 57.2, 80.7, 126.2, 132.2, 136.7, 147.2, 175.8, and 194.5. IR ν 1785 and 1670 cm^{-1}. UV λ_{max}^{MeOH} 226 nm (ε=6600)], **10** [colorless needles, mp 192—194 °C, 29.8 mg; 3%. Found: *m/z*, 310.1161 (M^+). Calcd for $C_{19}H_{18}O_4$: M, 310.1204. ^{1}H NMR δ=2.46 (H_j, br d, J=4.5 Hz), 2.67 (H_h, ddd, J=8.5, 4.5, 2 Hz), 3.19 (3H, s), 3.2 (H_c, m), 3.4 (H_r, m), 3.58 (H_f, dddm, J=7, 2, 1.5 Hz), 3.66 (H_n, ddt, J=8.5, 7.5, 1 Hz), 4.74 (H_g, dt, J=8.5, 1.5 Hz), 5.62 (H_a, ddd, J=11, 2, 0.5 Hz), 5.76 (H_k, ddd, J=11, 2, 1 Hz), 6.11 (H_q, tm, J=7.5 Hz), 6.16 (H_e, ddt, J=8.5, 7, 1 Hz), 6.50 (H_d, ddd, J=8.5, 7.5, 1.5 Hz), 6.51 (H_p, tm, J=7.5 Hz), 6.84 (H_m, ddm, J=11, 8.5 Hz), and 7.02 (H_b, dd, J=11, 8.5 Hz). ^{13}C NMR δ=39.3, 43.1, 49.1, 52.2, 54.9, 58.7, 60.8, 84.8, 118.1, 125.5, 127.1, 129.7, 130.4, 136.0, 138.1, 148.5, 152.2, 194.8, and 195.2. IR ν 1665 cm^{-1}. UV λ_{max}^{MeOH} 230 nm (ε=11300)], **11** [colorless crystals, mp 180—182 °C, 6 mg; 0.5%. Found: *m/z*, 310.1201 (M^+). ^{1}H NMR δ=2.4 (H_h, ddm, J=8.5, 4 Hz), 2.58 (H_j, dm, J=4 Hz), 3.10 (3H, s), 3.4 (H_c, br m), 3.43 (H_r, dm, J=6.5 Hz), 3.75 (H_n, ddt, J=8.5, 7.5, 1 Hz), 3.87 (H_f, dm, J=6.5 Hz), 4.65 (H_g, dd, J=8.5, 6.5 Hz), 5.79 (H_a, ddd, J=11, 2, 1 Hz), 5.93 (H_k, ddd, J=11, 2, 1 Hz), 5.94 (H_e, ddd, J=8.5, 7.5, 1 Hz), 6.18 (H_q, ddm, J=7.5, 6.5 Hz), 6.50 (H_d or H_p, ddd, J=8.5, 7.5, 1 Hz), 6.52 (H_p or H_d, ddd, J=8.5, 7.5, 1 Hz), 6.85 (H_b, dd, J=11, 8.5 Hz), and 6.91 (H_m, dd, J=11, 8.5 Hz). ^{13}C NMR δ=40.4, 43.7, 49.5, 52.4, 54.0, 59.4, 59.5, 85.0, 119.1, 125.9, 126.2, 130.4, 133.0, 137.8, 139.5, 148.6, 149.6, 195.2, and 195.4. IR ν 1662 cm^{-1}. UV λ_{max}^{MeOH} 224 nm (ε=11900)], **12** [a yellow oil, 42.4 mg; 4%. Found: *m/z*, 310.1193 (M^+).[20] ^{1}H NMR δ=2.48 (1H, br s), 2.51 (1H, d, J=7 Hz), 2.79 (1H, ddd, J=8.5, 7, 2 Hz), 3.33 (1H, underneath the MeO), 3.38 (3H, s), 3.80 (1H, dtd, J=7, 2, 1.5 Hz), 4.84 (1H, ddd, J=8.5, 2, 1 Hz), 5.06 (1H, dd, J=9, 4 Hz), 5.68 (1H, dd, J=11, 2 Hz), 5.68 (1H, br d, J=6 Hz), 6.0—6.3 (3H, m), 6.36 (1H, dd, J=9, 6 Hz), 6.60 (1H, tm, J=8 Hz), and 7.03 (1H, dd, J=11, 8 Hz). ^{13}C NMR δ=38.6, 47.4, 51.3, 51.8, 54.0, 59.1, 80.0, 97.1, 121.4, 124.7, 126.8, 128.1, 129.5, 130.1, 134.1, 135.7, 149.3, 152.6, and 193.8. IR ν 1670 and 1633 cm^{-1}], **13** [a yellow oil, 36.1 mg; 3%. Found: *m/z*, 310.1210 (M^+).

^{1}H NMR δ=2.51 (1H, t, J=7.5 Hz), 3.1—3.6 (3H, m), 3.45 (3H, s), 3.78 (1H, dtd, J=7, 2, 1.5 Hz), 4.71 (1H, ddd, J=8.5, 2, 1 Hz), 5.00 (1H, dd, J=9, 3 Hz), 5.7 (1H, br m), 5.71 (1H, dd, J=11, 2 Hz), 6.0—6.2 (3H, m), 6.28 (1H, ddt, J=9.5, 7, 1 Hz), 6.58 (1H, tm, J=7.5 Hz), and 7.10 (1H, dd, J=11, 8.5 Hz). ^{13}C NMR ν=39.1, 42.6, 45.5, 50.2, 51.7, 58.8, 80.1, 99.9, 118.3, 123.9, 128.2, 128.3, 129.4, 130.2, 131.6, 135.5, 152.4, 152.7, and 193.8. IR ν 1670 and 1632 cm^{-1}], and **14** [a yellow oil, 37.4 mg; 3%. Found: *m/z*, 310.1202 (M$^+$). ^{1}H NMR δ=2.4—2.6 (2H, m), 2.68 (1H, dd, J=5, 1 Hz), 3.35 (3H, s), 3.5 (1H, br m), 4.00 (1H, tdd, J=7, 2, 1 Hz), 4.80 (1H, dd, J=8.5, 7 Hz), 5.10 (1H, ddd, J=8.5, 4.5, 1 Hz), 5.67 (1H, d, J=5.5 Hz), 5.98 (1H, ddd, J=11, 2, 1 Hz), 6.05 (1H, ddd, J=7.5, 2, 1 Hz), 6.1—6.5 (3H, m), 6.56 (1H, ddd, J=8, 7, 1 Hz), and 6.98 (1H, dd, J=11, 8.5 Hz). ^{13}C NMR δ=39.9, 48.0, 51.9, 52.1 (2C), 56.8, 78.8, 96.5, 121.4, 124.6, 125.2, 126.7, 128.4, 129.5, 132.9, 134.5, 139.8, 149.4, and 194.2. IR ν 1670 and 1633 cm^{-1}], and **15** [a yellow oil, 22.6 mg; 2%. Found: *m/z*, 310.1205 (M$^+$). ^{1}H NMR δ=2.69 (1H, dd, J=7.5, 6 Hz), 2.90 (1H, ddd, J=8.5, 6, 5 Hz), 3.3—3.7 (2H, m), 3.42 (3H, s), 3.98 (1H, dddd, J=7.5, 7, 2, 1 Hz), 4.61 (1H, dd, J=8.5, 7 Hz), 5.00 (1H, ddm, J=9, 3 Hz), 5.66 (1H, dm, J=5 Hz), 5.98 (1H, ddd, J=11, 2, 1 Hz), 6.0—6.4 (4H, m), 6.61 (1H, ddd, J=9, 7, 1 Hz), and 6.97 (1H, dd, J=11, 8.5 Hz). ^{13}C NMR δ=40.4, 42.7, 45.8, 48.5, 51.8, 56.9, 78.8, 99.6, 119.1, 123.8, 125.3, 128.2, 129.2, 131.7, 132.7, 139.7, 150.0, 153.1, and 194.5. IR ν 1670 and 1632 cm^{-1}].

b) An IB solution (5 cm^3) of **1** (67 mg) and **3** (613 mg) was heated at 130 °C for 10 h in a sealed tube. Silica-gel column chromatography of the mixture afforded recovered **1** [14.6 mg; 22%], **7** [11.8 mg; 13%], and **8** [2.6 mg; 3%].

Diels-Alder Reaction of 1 with 4. a) An IB solution (5 cm^3) of **1** (94 mg) and **4** (126 mg) was heated at 130 °C for 10 h under 3000 bar. The silica-gel column chromatography afforded, together with the recovered **1** [59.2 mg; 63%], a mixture of products, whose HPLC purification gave **16** [colorless crystals, mp 82—84 °C, 6.4 mg; 8%. Found: *m/z*, 234.0897 (M$^+$). Calcd for $C_{13}H_{14}O_4$: M, 234.0892. ^{1}H NMR δ=3.24 (3H, s), 3.54 (3H, s), 3.69 (1H, t, J=8.5 Hz), 3.77 (1H, dtd, J=7, 2, 1.5 Hz), 4.58 (1H, d, J=2 Hz), 5.82 (1H, dd, J=11, 2 Hz), 6.06 (1H, tt, J=7, 1 Hz), 6.09 (1H, s), 6.36 (1H, ddd, J=8.5, 7, 1.5 Hz), and 7.00 (1H, dd, J=11, 8.5 Hz). ^{13}C NMR δ=42.2, 51.6, 57.9, 60.4, 81.4, 94.1, 125.8, 128.2, 130.7, 136.1, 140.5, 152.5, and 193.5. IR ν 1660 and 1090 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$ 220 nm (ε=8800) and 302 (850)] and **17** [colorless crystals, mp 126—128 °C, 21.2 mg; 28%. Found: C, 66.25; H, 5.97%; *m/z*, 234.0922. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.04%. ^{1}H NMR δ=3.23 (3H, s), 3.52 (3H, s), 3.52 (1H, dddt, J=9, 7, 1.5, 1 Hz), 3.95 (1H, dddd, J=7.5, 6.5, 2, 1 Hz), 4.58 (1H, dd, J=6.5, 1.5 Hz), 5.80 (1H, ddd, J=11, 2, 1 Hz), 5.97 (1H, ddd, J=8.5, 7.5, 1 Hz), 6.03 (1H, s), 6.59 (1H, ddd, J=8.5, 7, 1 Hz), and 6.89 (1H, dd, J=11, 9 Hz). ^{13}C NMR δ=44.5, 51.9, 56.0, 57.8, 81.5, 92.8, 123.0, 127.4, 131.7, 137.8, 140.8, 148.8, and 193.7. IR ν 1665 and 1080 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$ 221 nm (ε=7600) and 316 (250)].

b) An IB solution (1 cm^3) of **1** (31.6 mg) and **4** (38.9 mg) was heated at 130 °C in a sealed tube. Silica-gel column chromatography of the mixture afforded, other than the recovered **1** [21.3 mg; 67%] and **4** [19 mg; 49%], a complicated mixture of products, 3.8 mg, whose HPLC revealed more than ten compounds.

Thermal Rearrangement of 13. A benzene-d_6 (C_6D_6) solution (0.3 cm^3) of **13** (13 mg) was heated in a sealed NMR tube at 100 °C for 5 d. The HPLC of the mixture afforded **10** [0.3 mg; 3%], which was identical with the authentic sample prepared directly from **1** and **3**.

Thermal Rearrangement of 15. A C_6D_6 solution (0.3 cm^3) of **15** (9 mg) was similarly heated in a sealed tube at 100 °C for 5 d. The HPLC of the mixture afforded **11** [0.1 mg; 1%], identical with the authentic sample.

Attempted Thermal Rearrangement of 12 and 14. An each C_6D_6 solution (0.3 cm^3) of **12** (17 mg) and **14** (27 mg) was heated in a sealed NMR tube at 100 °C for 5 d. Despite a careful NMR inspection, every chromatographic fraction gave no identifiable product.

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