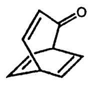
August, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 2257—2263 (1990) 2257

High-Pressure Cycloaddition of Tropones to Ethoxyethene. An Occurrence of [4+2] and [8+2] Cycloadditions

Akira Mori,* Zhi-Hong Li,† and Hitoshi Takeshita*
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
(Received March 12, 1990)

Although thermal cycloaddition of tropone to ethoxyethene under ordinary pressure conditions is synthetically impractical, the reaction was greatly improved under 10000 bar to give six products with 95% conversion (1 bar=10^5 Pa): the major products obtained in 66% yield were 9α- and 9β-ethoxybicyclo[3.2.2]nona-3,6-dien-2-ones, Diels–Alder adducts, which were accompanied by other two 8-ethoxy derivatives and two [8+2] cycloadducts. 2-Methoxy- and 2-chlorotropones similarly gave better results under high-pressure conditions. The ^{13}C NMR spectra of these Diels–Alder adducts provided useful information regarding structure elucidations.

Recently, the thermal cycloaddition of tropones has again become a focus of much attention regarding various aspects; in 1987 we reported[1)] an improved synthesis of homobarrelenone (**A**)[2)] by means of a high-pressure Diels-Alder reaction of tropone to 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene and subsequent fragmentation, which opened a general route for synthesizing substituted derivatives of **A**.



A

We have now examined a reaction of tropones to ethoxyethene (**1**) in order to prepare 9- or 8-ethoxybicyclo[3.2.2]nona-3,6-dien-2-ones, dihydrohomobarrelenones. It is well known that **1** polymerizes easily under ordinary conditions, and that high-pressure cycloaddition greatly improves the reaction by suppressing the radical process.[3)]

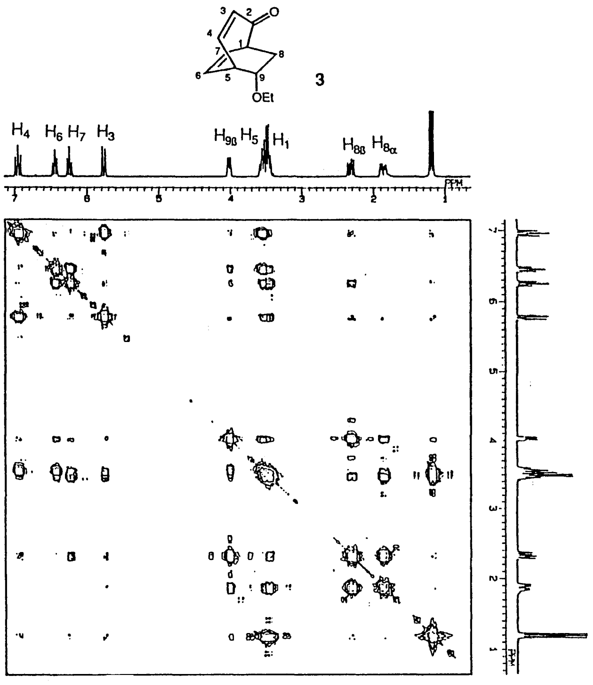


Fig. 1. The H-H COSY Spectrum of **3**.

Results and Discussion

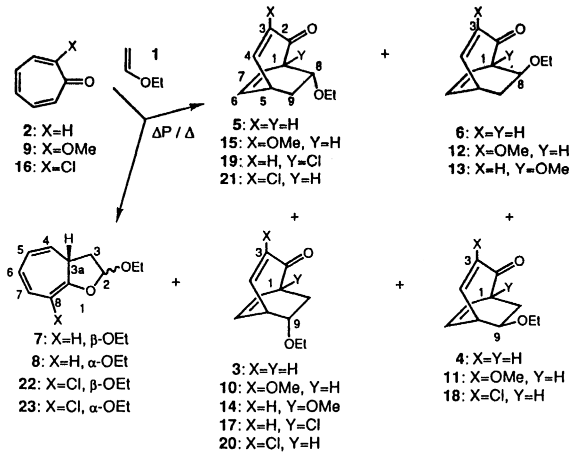
Thermal High-Pressure Cycloaddition. When **1** and tropone (**2**) were heated at 120 °C under 10000 bar for 10 h, 95% of **2** was consumed to give 1 : 1-adducts (**3**—**8**).

The major products, **3** and **4**, obtained in 38 and 28% yields, respectively, were 9α- and 9β-ethoxybicyclo[3.2.2]nona-3,6-dien-2-ones in view of the NMR spectral similarity with the reported derivatives.[4)] However, in the ^{1}H NMR of **3**, the methylene proton signal of the ethoxyl group appeared at ca. δ=3.5 as overlapping multiplets with other two proton signals, preventing an unambiguous assignment by first-order analysis; thus, two-dimensional H-H and C-H COSY experiments[5)] were carried out. According to the H-H COSY spectrum of **3** (Fig. 1), mutually-correlated signals, a methine proton signal at δ=4.01 and the lower component of the overlapped signal at δ=3.5, respectively, showed correlations to those at δ=1.87, 2.32, and 6.44.

Therefore, the signal in the lower part of the overlapping multiplets was assigned to be the signal of the C-5 methine proton; the hydrogen on the ethereal carbon, appearing at δ=4.01, is therefore adjacent to C-5 (i.e, C-9). Furthermore, the C-9 methine proton signal behaved as a doublet with additional small splittings; this was only possible for the β-methine proton at C-9, whose vicinal coupling constant with the signal of the C-5 proton should be small in accordance with a stereomolecular model inspection.[4)]

In the ^{1}H NMR of **4**, the corresponding methine proton signal appeared as a doublet of doublets of doublets at δ=3.88, and its coupling constant, J=4.4 Hz, with the adjacent C-5 proton eliminated the structure other than that depicted.

The other Diels-Alder adducts, **5** and **6**, were 8α-



Scheme 1.

and 8*β*-ethoxy derivatives. Their structures were similarly deduced from the ^{1}H NMR spectra; i.e. in **5**, the signal ascribable to the proton on the ethereal carbon appeared as a doublet of doublets at δ=4.03 with coupling constants of 8.4 and 4.4 Hz, and the C-1 methine proton signal was a doublet of doublets at δ=3.75 (J=7.3, 1.8 Hz). Therefore, **5** is 8*α*-ethoxy and **6** is 8*β*-ethoxy derivatives, respectively.

The remaining **7** and **8** were stereoisomeric [8+2] cycloadducts, and the stereochemistry was differentiated by coupling sequences; in the ^{1}H NMR spectrum of **7**, the *α*-oriented methine proton of the ethereal carbon, C-2, at δ=5.43, appeared as a doublet of doublets, J=5.5 and 1.1 Hz, and *β*-proton of the adjacent methylene group at C-3 coupled to C-2 proton with J=1.1 Hz showed a large vicinal coupling constant, J=8.1 Hz, with the methine proton at the ring juncture, C-3a. Therefore, the proton on the ring-juncture has *β*-orientation. The nuclear Overhauser effect (NOE) further supported this conclusion; by irradiating frequencies corresponding to the C-4 olefinic proton signal, the proton signals of the *β*-proton at C-3 showed an enhancement, ca. 4%. On the other hand, the methine proton on the ethereal carbon, C-2, showed a signal at δ=5.53 as a doublet of doublets, J=5.5 and 1.8 Hz, of which the larger coupling was assigned to be with the *β*-proton on the C-3. The large coupling constant between the *β*-proton on C-3 and the angular *β*-proton at C-3a led us to formulate the structure as depicted. Though the NOE experiments with **8** showed no contradiction to this, overlapping of the observed signals provided insufficient information to draw a conclusion.

Similarly, 2-methoxytropone (**9**) and **1** also gave six stereoisomeric 1 : 1-Diels-Alder adducts (**10**—**15**), but no [8+2] cycloadduct was detectable in this case. The major class of products **10**—**12**, and **15**, was 3-substituted derivatives, since they showed three olefinic proton signals; 1-methoxy derivatives, **13** and **14**, were obtained only in combined yield of 11.5%. Their structures were elucidated by NMR spectral evidence. Namely, 9*α*-ethoxy-3-methoxy derivative, **10**, showing the signal of the 9*β*-proton at δ=3.97 as a doublet of triplets, J=8.1 and 1.8 Hz, was similar to that of **3**, at δ=4.01 (dm, J=8.1 Hz). This type of similarity was consistently observed between the Diels-Alder adducts from **2** and **9**. For example, in the ^{1}H NMR of 8*β*-ethoxy-1-methoxy derivative, **13**, the signal ascribable to the methine proton on the ethereal carbon appeared at δ=4.04 as a clear doublet of doublets, J=8.8 and 1.8 Hz. This difference in the splitting pattern is an evidence of the 1-methoxy derivative; usually, 8*β*-ethoxy derivatives reveal relatively large splittings of ca. 8 to 9 Hz and 5 to 6 Hz with an additional small splitting of ca. 2 to 3 Hz. A lack of the other splitting in **13** shows the presence of a substituent at C-1.

The reaction of 2-chlorotropone (**16**) and **1** proceeded quantitatively to afford five Diels-Alder adducts (**17**—**21**) and two [8+2] cycloadducts (**22** and **23**). Their structures were elucidated by the same principle as in the cases of **1** to **2** and **9**. For example, one of the major product, **18**, showed three olefinic proton signals, indicating a chlorine atom on the C-3 position. As can be seen in Table 1, its methine proton signal on the ethereal carbon appeared at δ=3.83 with spin-spin splittings of J=8.8, 5.1, and 4.7 Hz, of which the figure, 4.7 Hz, is assigned to be the coupling constant with the C-5-methine at δ=3.77 appearing as a doublet of doublets of doublets, J=9.1, 7.1 and 4.7 Hz. This clearly indicated **18** to be a 3-chloro-9*β*-ethoxy derivative. The next major product, **19**, had a 1-chloro-8*α*-ethoxy structure; the sig-

Table 1. ^{1}H NMR Chemical Shifts Data of Methine Proton Signals of the Ethereal Carbons

	8*α*-EtO	8*β*-EtO	9*α*-EtO	9*β*-EtO
H	4.03	3.98	4.01	3.88
	(dd, 8.4, 4.4)	(ddd, 8.8, 5.9, 2.7)	(dm, 8.1)	(ddd, 8.5, 5.5, 4.4)
1-MeO		4.04	3.95	
		(dd, 8.8, 1.8)	(dm, 8.1)	
1-Cl	3.88		3.97	
	(ddd, 8.4, 3.7, 1.1)		(dm, 8.1)	
3-MeO	4.02	3.95	3.97	3.79
	(ddt, 8.4, 4.8, 1.1)	(ddd, 9.2, 6.2, 2.9)	(dt, 8.1, 1.8)	(ddd, 8.1, 5.1, 4.0)
3-Cl	4.02		4.04	3.83
	(dd, 8.3, 4.8)		(dt, 8.1, 2.2)	(ddd, 8.7, 5.1, 4.7)

nal of proton on the ethereal carbon appeared as a doublet of doublets of doublets at δ=3.88 (J=8.4, 3.7, 1.1 Hz); the magnitude of the second splitting identified to be an α-ethoxy derivative, and the third splitting was identified to be a spin-spin splitting due to the C-5 methine proton. This kind of relationship between regio- and stereo-chemical preferences (1-chloro-8α- vs. 3-chloro-9β-) was frequently observed in the Diels-Alder reaction of troponoids[6] The product, **21**, which was obtained in very minute amounts via intensive high-pressure liquid chromatography, was identified to be the Diels-Alder adduct having a 3-chloro-8α-ethoxy-structure. In high-pressure liquid chromatograms there were three more Diels-Alder adducts, indicating the formation of all of the possible stereo- and regio-isomers. However, due to the limited amount available, no attempt was made to isolate them.

Substituent Effects of ^{13}C NMR Chemical Shifts of the Diels-Alder Adducts. Two decades ago we analyzed the ^{1}H NMR chemical shifts of a series of cyano derivatives of this group,[4] and these data were occasionally employed to deduce the structures of the related compounds.[7]

As already mentioned, several methine proton signals in the present series were obscured by overlapping with other signals, and made first-order analysis difficult. In view of the rigid carbocyclic framework of the bicyclo[3.2.2]nonadienones, the ^{13}C NMR data must provide direct and clear information; we thus made an unambiguous assignment of ^{13}C chemical shifts of the major products, **3** and **4**, derived from parent tropone, **2**, by means of C-H COSY measurements (Figs. 2 and 3).

After establishing the assignments of ^{13}C chemical shifts of **3** and **4**, mutual comparisons allowed a full assignment of all ^{13}C chemical shifts of the derivatives. Table 2 shows these figures together with the chemical shift differences of each carbon of chloro and methoxy derivatives calculated therefrom.

Among the derivatives, a large substituent effect on the chemical shift was recognized in a neighborhood linked within two covalent bonds; for example, upon the introduction of substituents into the C-1 position, the chemical shifts of the carbonyl carbon caused large

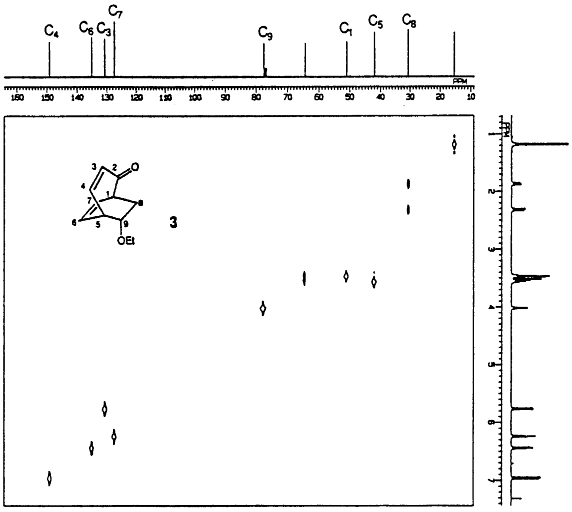


Fig. 2. The C-H COSY Spectrum of **3**.

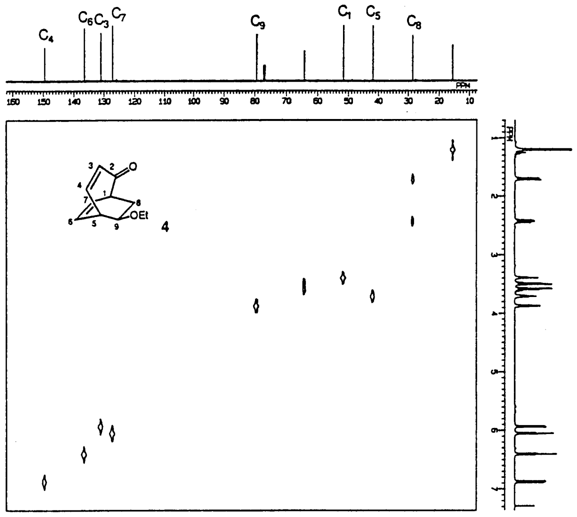


Fig. 3. The C-H COSY Spectrum of **4**.

Table 2. The ^{13}C NMR Chemical Shifts Assignment of Ethoxybicyclo[3.2.2]nonadienes

No.	8α-Ethoxy derivatives				8β-Ethoxy derivatives		
	5 H	**19** 1-Cl	**15** 3-MeO	**21** 3-Cl	**6** H	**13** 1-MeO	**12** 3-MeO
C-1	58.9	83.9 (+25.0)[a)]	57.8 (−1.1)	57.7 (−1.2)	57.7	92.5 (+34.8)[a)]	56.6 (−1.1)
C-2	195.7	187.7 (−8.0)	191.3 (−4.4)	188.4 (−7.3)	195.7	192.5 (−3.2)	191.3 (−4.4)
C-3	129.4	131.9 (+2.5)	150.4 (+21.0)	132.0 (+2.6)[a)]	131.0	130.0 (−1.0)	152.3 (+21.3)[a)]
C-4	153.9	154.3 (+0.4)	120.3 (−33.6)	150.0 (−3.9)	153.5	150.9 (−2.6)	120.3 (−33.2)
C-5	35.5	35.4 (−0.1)	35.7 (+0.2)	34.9 (−0.6)	36.7	36.3 (−0.4)	36.6 (−0.1)
C-6	138.4	135.7 (−2.7)	139.8 (+1.4)	138.3 (−0.1)	139.8	138.0 (−1.8)	140.6 (+0.8)
C-7	124.8	127.2 (+2.4)	124.0 (−0.8)	124.9 (+0.1)	125.3	128.8 (+3.5)	124.6 (−0.7)
C-8	75.7	78.6 (+2.9)	75.6 (−0.1)	75.1 (−0.6)	75.1	78.5 (+3.4)	74.9 (−0.2)
C-9	34.8	33.7 (−1.1)	32.0 (−2.8)	34.9 (+0.1)	36.4	34.9 (−1.5)	33.6 (−2.8)
Et	15.4	15.2	15.4	15.3	15.3	15.5	15.2
	64.8	67.9	64.7	64.9	64.6	66.1	64.6
Me			54.7			52.8	54.9

Table 2. (Continued)

No.	9α-Ethoxy derivatives					9β-Ethoxy derivatives		
	3 H	**14** 1-MeO	**10** 3-MeO	**17** 1-Cl	**20** 3-Cl	**4** H	**11** 3-MeO	**18** 3-Cl
C-1	51.1	85.7 (+34.6)[a]	50.3 (−0.8)	83.6 (+32.5)[a]	50.1 (−1.0)	51.7	50.5 (−1.2)	50.6 (−1.1)
C-2	197.3	194.5 (−2.8)	192.9 (−4.4)	188.0 (−9.3)	190.0 (−7.3)	197.6	193.3 (−4.3)	190.4 (−7.2)
C-3	130.9	130.9 (0.0)	151.5 (+20.6)[a]	133.4 (+2.5)	133.3 (+2.4)[a]	131.0	151.5 (+20.5)[a]	133.1 (+2.1)[a]
C-4	149.2	147.8 (−1.4)	115.8 (−33.4)	148.6 (−0.6)	145.5 (−3.7)	149.5	115.3 (−34.2)	146.2 (−3.3)
C-5	42.1	41.8 (−0.3)	39.0 (−3.1)	42.4 (+0.3)	41.8 (−0.3)	41.9	38.9 (−3.0)	42.0 (+0.1)
C-6	135.1	133.6 (−1.5)	136.5 (+1.4)	134.1 (−1.0)	135.2 (+0.1)	136.5	137.9 (+1.4)	136.5 (0.0)
C-7	127.6	129.4 (+1.8)	127.0 (−0.6)	128.9 (+1.3)	127.6 (0.0)	127.2	126.5 (−0.7)	127.2 (0.0)
C-8	30.7	35.5 (+4.8)	30.4 (−0.3)	41.1 (+10.4)	30.2 (−0.5)	28.6	28.1 (−0.5)	28.1 (−0.5)
C-9	77.8	75.2 (−2.6)	78.2 (+0.4)	76.2 (−1.6)	77.1 (−0.7)	79.5	78.4 (−1.1)	78.9 (−0.6)
Et	15.4	15.4	15.4	15.3	15.4	15.5	15.5	15.4
	64.5	64.5	64.4	64.7	64.6	64.4	64.2	64.5
Me		52.2	54.8				54.9	

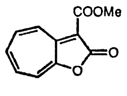
a) Figures were chemical shifts of carbons carrying the substituents.

Table 3. Pressure Effect for Product Distributions of the Reaction of **1** and Tropones (**2**, **9**, and **16**)

Tropones	Pressure/bar	[4+2] Exo		[4+2] Endo		[8+2]	[4+2]/[8+2]
		8β	9β	8α	9α		
2	1	4.1	26.3	2.1	35.0	32.5	ca. 2/1
2	10000	4.5	32.8	2.3	44.2	16.2	ca. 5/1
9	1	4.3	31.9	8.5	55.3	—	
9	10000	20.1	26.3	2.7	50.9	—	
16	1	—	21.7	19.2	—	59.6	ca. 2/3
16	10000	—	31.7	3.8	28.2	36.3	ca. 2/1

up-field shifts by steric compression, i.e., the chemical shift differences from those of parent ethoxy derivatives, Δδ, were ca. 3 for methoxy derivatives and 7—10 for chloro derivatives. The observed behavior upon introducing substituents into the C-3 position, being the α-position in the α,β-unsaturated keto system, were just as predicted. Other than these, almost all of the signals appeared within Δδ=ca. 3. Notable exceptions were the C-8 signals of 1-substituted derivatives, i.e, 1-chloro-9α-ethoxy derivative, **17** showed Δδ=+10.4, and 9α-ethoxy-1-methoxy derivative, **14** showed +4.8. These could be understood by the presence of the substituents at C-1. Thus, although we must sometimes be extremely careful, the ^{13}C NMR spectra can provide reliable information concerning structure elucidations.

Pressure Effect of the Cycloaddition. It is evident that the high-pressure conditions were effective for obtaining better results; in all cases, reactions under ordinary pressure conditions proceeded very slowly. For the reaction of **1** and **2** under ordinary pressure, a much longer time (i.e., ca. 100 h for 43% conversion of **2** at 100 °C) was required. However, there was a notable difference in product distributions: that is, the ratios of [4+2]/[8+2] were larger under high-pressure conditions for reactions with both **2** and **16** (Table 3). This is parallel to the pressure effect of the cycloaddition reaction of **1** to cyclohepta[*b*]furan-2-one derivatives (**B**).[8)]



B

It is now clear that the [4+2] cycloadducts formed in kinetically controlled fashion, but that the [8+2] cycloadducts were thermodynamic products.

Experimental

Elemental analyses were performed by Mrs. M. Miyazawa of this Institute, Kyushu University. The mps were measured with a Yanagimoto micro mp apparatus and are not corrected. The NMR spectra were measured by JEOL FX 100 and GSX 270H spectrometers in $CDCl_3$, unless otherwise specified, and the chemical shifts expressed were in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily materials using a JASCO IR-A 102 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

High-Pressure Diels-Alder Reaction of 1 and 2. A toluene solution (4 cm^3) of **1** (590 mg), **2** (424 mg), and hydroquinone (20 mg) was heated at 80 °C under 10000 bar for 12 h. The mixture was then separated by means of a silica-gel column and high-pressure liquid (Microporasil, EtOAc and hexane) chromatography to give the following products:

3: A colorless oil, 270 mg; 37.9%. Found: C, 73.81; H, 7.91%; M.W., 178.0995 (M^+). Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%; M.W., 178.0994. ^{1}H NMR δ=1.19 (3H, t, J=7.0 Hz), 1.87 (1H, m), 2.32 (1H, dd, J=13.9, 8.1 Hz), 3.4—3.6 (3H, m), 3.55 (1H, dd, J=9.2, 7.0 Hz), 4.01 (1H, dm, J=8.1 Hz), 5.77 (1H, ddd, J=11.0, 2.5, 0.7 Hz), 6.24 (1H, tm, J=8.4 Hz), 6.44 (1H, ddt, J=8.4, 7.0, 0.7 Hz), and 6.95 (1H, dd, J=11.0, 9.2 Hz). MS m/z: 179 (6), 178 (30), 149 (44), 133 (29), 132 (100), 131 (78), 121 (39), 107 (81), 103 (26), 91 (44), 77 (46), 44 (34), and 26 (37). IR: 3016, 2876, 1667, 1386, 1222, 1089, and 669 cm^{-1}. λ^{MeOH}_{max}=237 nm (ε=4400) and 342 (130).

4: A colorless oil, 200 mg; 28.1%. Found: M.W., 178.0989 (M^+). Calcd for $C_{11}H_{14}O_2$; 178.0994. ^{1}H NMR δ=1.20 (3H, t, J=7.0 Hz), 1.70 (1H, dd, J=14.3, 5.5 Hz), 2.42 (1H, ddd, J=14.3, 8.8, 7.0 Hz), 3.39 (1H, ddd, J=7.3, 7.0, 0.7 Hz), 3.49 (1H, dq, J=9.5, 7.0 Hz), 3.59 (1H, dq, J=9.5, 7.0 Hz), 3.70 (1H, ddd, J=8.4, 7.3, 4.4 Hz), 3.88 (1H, ddd, J=8.8, 5.5, 4.4 Hz), 5.93 (1H, dd, J=11.0, 2.2 Hz), 6.05 (1H, dd, J=8.1, 7.3 Hz), 6.40 (1H, ddd, J=8.1, 7.3, 1.1 Hz), and 6.87 (1H, dd, J=11.0, 8.4 Hz). MS m/z: 179 (8), 178 (29), 149 (36), 132 (82), 107 (100), 91 (38), 77 (38), 44 (28), and 26 (28). IR : 3048, 2972, 2870, 1668, 1387, 1100, and 733 cm^{-1}. UV λ^{MeOH}_{max}=232 nm (ε=3600).

5: A colorless oil, 14 mg; 2.0%. Found: M.W., 178.0994 (M^+). Calcd for $C_{11}H_{14}O_2$: 178.0994. ^{1}H NMR δ=1.19 (3H, t, J=7.0 Hz), 1.65 (1H, dt, J=13.2, 4.4 Hz), 2.51 (1H, ddd, J=13.2, 8.4, 1.8 Hz), 3.2—3.3 (1H, br m, $W_{h_{1/2}}$=23 Hz), 3.44 (1H, dq, J=9.5, 7.0 Hz), 3.57 (1H, dq, J=7.5, 7.0 Hz), 3.75 (1H, dd, J=7.3, 1.8 Hz), 4.03 (1H, dd, J=8.4, 4.4 Hz), 5.68 (1H, dd, J=11.0, 1.8 Hz), 6.07 (1H, dd, J=8.4, 7.3 Hz), 6.67 (1H, t, J=8.4 Hz), and 7.07 (1H, dd, J=11.0, 8.8 Hz). MS m/z: 178 (100), 149 (52), 132 (64), 131 (56), 107 (69), 91 (28), 78 (58), 77 (48), 72 (87), 55 (31), 44 (72), 43 (72), 43 (37), and 39 (26). IR: 3044, 2970, 2930, 1666, 1634, 1385, 1097, 716, and 676 cm^{-1}. λ^{MeOH}_{max}=228 nm (ε=6000).

6: A colorless oil, 28 mg; 3.9%. Found: M.W., 178.0996 (M^+). Calcd for $C_{11}H_{14}O_2$: 178.0994. ^{1}H NMR δ=1.13 (3H, t, J=7.0 Hz), 1.91 (1H, dm, J=13.6 Hz), 2.26 (1H, ddd, J=13.6, 8.8, 5.1 Hz), 3.25—3.35 (1H, br m, $W_{h_{1/2}}$=25 Hz), 3.41 (1H, dq, J=9.2, 7.0 Hz), 3.67 (1H, dq, J=9.2, 7.0 Hz), 3.98 (1H, ddd, J=8.8, 5.9, 2.7 Hz), 4.05 (1H, ddm, J=7.3, 5.9 Hz), 5.85 (1H, dd, J=11.0, 1.4 Hz), 5.99 (1H, dd, J=7.7, 7.3 Hz), 6.54 (1H, dd, J=8.1, 7.7 Hz), and 7.16 (1H, dd, J=11.0, 8.8 Hz). IR: 3040, 2926, 2866, 1730, 1663, 1633, 1387, 1249, 1098, and 757 cm^{-1}. UV λ^{MeOH}_{max}=225 nm (ε=4100) and 290 (600).

7: A colorless oil, 28 mg; 3.9%. Found: M.W., 178.0991 (M^+). Calcd for $C_{11}H_{14}O_2$; 178.0994. ^{1}H NMR δ=1.22 (3H, t, J=7.7 Hz), 2.13 (1H, ddd, J=13.5, 8.1, 5.5 Hz), 2.52 (1H, dd, J=13.5, 9.5 Hz), 2.93 (1H, dddd, J=9.5, 8.1, 3.3, 2.2 Hz), 3.56 (1H, dq, J=9.5, 7.0 Hz), 3.82 (1H, dq, J=9.5, 7.0 Hz), 4.89 (1H, dd, J=9.5, 3.3 Hz), 5.43 (1H, dd, J=5.5, 1.1 Hz), 5.72 (1H, dm, J=6.6 Hz), 6.07 (1H, ddd, J=9.5, 5.9, 2.2 Hz), 6.20 (1H, dd, J=11.0, 5.9 Hz), and 6.35 (1H, dd, J=11.0, 6.6 Hz). ^{13}C NMR δ=15.1, 38.5, 38.7, 63.9, 97.3, 106.5, 122.9, 124.0, 127.0, 128.6, and 153.8. MS m/z: 179 (14), 178 (100), 149 (56), 133 (36), 132 (83), 131 (95), 121 (56), 110 (98), 107 (71), 105 (48), 103 (35), 91 (44), 78 (46), 77 (57), 73 (90), 72 (63), 45 (72), 44 (64), 43 (32), and 26 (46). IR: 3014, 2976, 2930, 1647, 1544, 1505, 1379, 1346, 1155, 1099, 978, 918, and 710 cm^{-1}. λ^{MeOH}_{max}=212 nm (ε=11500), 265 (3000), 289 (3500), and 315 (2200).

8: A colorless oil, 71 mg; 10.0%. Found: M.W., 178.0991 (M^+). Calcd for $C_{11}H_{14}O_2$: 178.0994. ^{1}H NMR δ=1.18 (3H, t, J=7.3 Hz), 2.18 (1H, dt, J=12.7, 1.8 Hz), 2.55 (1H, ddm, J=10.3, 3.3 Hz), 2.60 (1H, ddd, J=12.7, 10.3, 5.5 Hz), 3.50 (1H, dq, J=9.5, 7.3 Hz), 3.75 (1H, dq, J=9.5, 7.3 Hz), 5.11 (1H, dd, J=9.2, 3.3 Hz), 5.53 (1H, dd, J=5.5, 1.8 Hz), 5.65 (1H, d, J=6.2 Hz), 6.07 (1H, dd, J=9.2, 5.5 Hz), 6.25 (1H, dd, J=11.0, 5.5 Hz), and 6.42 (1H, dd, J=11.0, 6.2 Hz). ^{13}C NMR δ=15.1, 37.1, 39.3, 64.2, 95.7, 107.4, 123.9, 124.2, 126.1, 129.2, and 152.4. IR: 3014, 2976, 1642, 1378, 1350, 1161, 1111, 951, 891, and 713 cm^{-1}. MS m/z: 179 (10), 178 (79), 149 (45), 132 (71), 131 (100), 121 (55), 118 (38), 107 (70), 105 (32), 103 (34), 91 (59), 78 (54), 77 (59), 73 (36), 72 (55), 44 (66), 43 (34), and 26 (50). UV λ^{MeOH}_{max}=265 nm (ε=2300), and 288 (2600).

High-Pressure Diels-Alder Reaction of 1 and 9. Similarly, a toluene solution (4 cm^3) of **1** (600 mg) and **9** (250 mg) was heated at 120 °C under 10000 bar for 10 h. The mixture was then separated on a silica-gel column and high-pressure liquid chromatography to give the following products:

10: Colorless crystals, mp 64—65 °C, 53 mg; 13.9%. Found: C, 69.21; H, 7.77%. Calcd for $C_{12}H_{16}O_3$; C, 69.21; H, 7.74%. ^{1}H NMR δ=1.18 (3H, t, J=7.0 Hz), 1.83 (1H, ddm, J=14.7, 6.2 Hz), 2.36 (1H, dd, J=14.7, 8.1 Hz), 3.4—3.65 (4H, m), 3.55 (3H, s), 3.97 (1H, dt, J=8.1, 1.8 Hz), 5.92 (1H, d, J=9.9 Hz), 6.23 (1H, t, J=8.1 Hz), and 6.51 (1H, dd, J=8.1, 7.3 Hz). MS m/z: 208 (100), 179 (22), 162 (29), 136 (94), 118 (27), 107 (79), 91 (27), 77 (27), and 28 (19). IR: 3040, 2966, 2872, 1681, 1637, 1616, 1367, 1225, 1118, 1038, 1033, 837, 783, and 770 cm^{-1}. UV λ^{MeOH}_{max}=239 nm (ε=2400) and 279 (3500).

11: A colorless oil, 48 mg; 11.9%. Found: M.W., 208.1096 (M^+). Calcd for $C_{12}H_{16}O_3$: 208.1098. ^{1}H NMR δ=1.20 (3H, t, J=7.0 Hz), 1.63 (1H, dd, J=14.3, 5.1 Hz), 2.37 (1H, ddd, J=14.3, 8.8, 7.1 Hz), 3.4—3.6 (3H, m), 3.59 (3H, s), 3.69 (1H, ddd, J=9.2, 8.4, 4.0 Hz), 3.79 (1H, ddd, J=8.8, 5.1, 4.0 Hz), 5.83 (1H, d, J=9.2 Hz), 6.03 (1H, dd, J=8.4, 7.7 Hz), and 6.48 (1H, td, J=8.4, 1.1 Hz). MS m/z: 208 (100), 162 (27), 136 (79), 107 (68), 105 (33), 91 (28), 79 (24), 77 (28), and 26 (21). IR: 3048, 2972, 2872, 1731, 1682, 1637, 1620, 1444, 1372, 1220, 1092, and 739 cm^{-1}. UV λ^{MeOH}_{max}=226 nm (ε=1800) and 276 (2000).

12: A colorless oil, 28 mg; 6.7%. Found: M.W., 208.1096 (M^+). Calcd for $C_{12}H_{16}O_3$: 208.1098. ^{1}H NMR δ=1.12 (3H, t, J=7.0 Hz), 1.83 (1H, dt, J=13.6, 2.9 Hz), 2.22 (1H, ddd, J=13.6, 9.2, 4.8 Hz), 3.39 (1H, dq, J=9.2, 7.0 Hz), 3.3—3.5 (1H, m), 3.55 (3H, s), 3.68 (1H, dq, J=9.2, 7.0 Hz), 3.95 (1H, ddd, J=9.2, 6.2, 2.9 Hz), 4.20 (1H, dd, J=7.0, 6.2 Hz), 5.96 (1H, ddd, J=8.1, 7.0, 1.1 Hz), 6.14 (1H, d, J=9.5 Hz), and 6.61 (1H, dd, J=8.1, 7.3 Hz). MS m/z: 208 (49), 136 (100), 118 (19), 107 (33), and 91 (17). IR: 3050, 2970, 2870, 1728, 1681, 1636, 1622, 1372, 1241, 1128, 1103, 1028, and 746 cm^{-1}. UV λ^{MeOH}_{max}=229 nm (ε=2300) and 277 (2600).

13: A colorless oil, 10 mg; 2.4%. Found: M.W., 208.1092 (M^+). Calcd for $C_{12}H_{16}O_3$: 208.1098. ^{1}H NMR δ=1.11 (3H, t, J=7.0 Hz), 1.91 (1H, dm, J=13.6 Hz), 2.16 (1H, ddd, J=13.6, 8.8, 4.4 Hz), 3.3 (1H, br m, $W_{h_{1/2}}$=23 Hz), 3.56 (1H, dq, J=9.2, 7.0 Hz), 3.58 (3H, s), 3.69 (1H, dq, J=9.2, 7.0 Hz), 4.04 (1H, dd, J=8.8, 1.8 Hz), 5.87 (1H, d, J=11.0 Hz), 5.98 (1H, dd, J=9.2, 1.1 Hz), 6.56 (1H, dd, J=9.2, 7.3 Hz), and 7.04 (1H, dd, J=11.0, 8.4 Hz). MS m/z: 208 (100), 179 (37), 161 (68), 136 (48), 131 (35), 108 (97), 99 (33), 91 (29), 55 (27), and 26 (26). IR: 2972, 2872, 1732, 1687, 1375, and 1103 cm^{-1}. UV λ^{MeOH}_{max}=224 nm (ε=3400).

14: A colorless oil, 38 mg; 9.1%. Found: M.W., 208.1100 (M$^+$). Calcd for $C_{12}H_{16}O_3$: 208.1098. ^{1}H NMR δ=1.19 (3H, t, J=7.0 Hz), 2.00 (1H, dm, J=14.0 Hz), 2.46 (1H, ddd, J=14.0, 8.1, 1.1 Hz), 3.4—3.8 (3H, m), 3.49 (3H, s), 3.95 (1H, dm, J=8.1 Hz), 5.81 (1H, d, J=11.0 Hz), 6.18 (1H, dm, J=8.8 Hz), 6.43 (1H, ddd, J=8.8, 7.0, 1.1 Hz), and 6.91 (1H, dd, J=11.0, 8.8 Hz). MS *m/z*: 208 (86), 179 (100), 164 (44), 135 (48), 119 (36), 109 (39), 108 (54), 91 (74), 77 (35), 55 (39), 39 (34), and 26 (30). IR: 3044, 2972, 2876, 1735, 1681, 1376, 1348, 1214, 1105, 1080, and 713 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=231 nm ($\varepsilon$=3800).

15: A colorless oil, 5 mg; 1.2%. Found: M.W., 208.1097 (M$^+$). Calcd for $C_{12}H_{16}O_3$: 208.1098. ^{1}H NMR δ=1.18 (3H, t, J=7.0 Hz), 1.60 (1H, dt, J=13.2, 4.8 Hz), 2.45 (1H, ddd, J=13.2, 8.4, 2.2 Hz), 3.3 (1H, m, $W_{h_{1/2}}$=24 Hz), 3.43 (1H, dq, J=9.5, 7.0 Hz), 3.52 (3H, s), 3.57 (1H, dq, J=9.5, 7.0 Hz), 3.90 (1H, d, J=7.3 Hz), 4.02 (1H, ddt, J=8.4, 4.8, 1.1 Hz), 6.04 (1H, d, J=9.5 Hz), 6.05 (1H, ddt, J=8.1, 7.3, 1.1 Hz), and 6.73 (1H, dd, J=8.1, 7.7 Hz). MS *m/z*: 208 (36), 136 (100), 107 (42), 105 (20), 91 (16), and 77 (14). IR: 2972, 1734, 1680, 1375, 1163, 1102, 1028, and 749 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=223 nm ($\varepsilon$=1600, sh) and 278 (1000).

High-Pressure Diels-Alder Reaction of 1 with 16. A toluene solution (4 cm^3) of **1** (580 mg) and **16** (282 mg) was heated at 100 °C under 10000 bar for 25 h. The mixture was then similarly fractionated to give the following products:

17: A colorless oil, 3 mg; 0.7%. Found: M.W., 212.0602 (M$^+$). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: 212.0603. ^{1}H NMR δ=1.19 (3H, t, J=7.0 Hz), 2.34 (1H, dm, J=14.7 Hz), 2.79 (1H, ddd, J=14.7, 8.1, 0.7 Hz), 3.49 (2H, q, J=7.0 Hz), 3.5—3.6 (1H, m), 3.97 (1H, dm, J=8.1 Hz), 5.94 (1H, d, J=11.4 Hz), 6.21 (1H, d, J=8.8 Hz), 6.45 (1H, ddd, J=8.4, 7.0, 1.1 Hz), and 6.97 (1H, dd, J=11.4, 8.8 Hz). MS *m/z*: 214 (M$^+$ for ^{37}Cl, 10), 212 (M$^+$ for ^{35}Cl, 30), 183 (27), 177 (100), 166 (31), 149 (42), 131 (85), 112 (39), 91 (49), 77 (31). IR: 3036, 2974, 2876, 1691, 1379, 1348, 1102, 1080, 930, and 622 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=220 nm ($\varepsilon$=4100).

18: A colorless oil, 134 mg; 31.4%. Found: C, 61.70; H, 6.40%; M.W., 212.0603 (M$^+$ for ^{35}Cl). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: C, 62.12; H, 6.16%; M.W., 212.0603. ^{1}H NMR δ=1.20 (3H, t, J=7.2 Hz), 1.69 (1H, dd, J=14.7, 5.1 Hz), 2.40 (1H, ddd, J=14.7, 8.8, 7.1 Hz), 3.45 (1H, dq, J=9.1, 7.2 Hz), 3.56 (1H, dq, J=9.1, 7.2 Hz), 3.66 (1H, t, J=7.1 Hz), 3.77 (1H, ddd, J=9.1, 7.1, 4.7 Hz), 3.83 (1H, ddd, J=8.8, 5.1, 4.7 Hz), 6.09 (1H, dd, J=8.3, 7.1 Hz), 6.45 (1H, ddd, J=8.3, 7.1, 1.2 Hz), and 7.18 (1H, d, J=9.1 Hz). MS *m/z*: 214 (M$^+$ for ^{37}Cl, 17), 212 (M$^+$ for ^{35}Cl, 52), 183 (58), 177 (100), 166 (98), 141 (54), 131 (39), 91 (52), 72 (83), 44 (59), and 26 (33). IR: 3052, 2972, 2872, 1687, 1637, 1604, 1371, 1338, 1103, 945, and 726 cm^{-1}. $\lambda_{\max}^{\mathrm{MeOH}}$=230 nm (4000, sh) and 254 (4800).

19: A colorless oil, 13 mg; 3.1%. Found: M.W., 212.0603 (M$^+$). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: 212.0603. ^{1}H NMR δ=1.21 (3H, t, J=7.0 Hz), 1.91 (1H, ddd, J=13.6, 5.1, 3.7 Hz), 2.53 (1H, ddd, J=13.6, 8.4, 1.8 Hz), 3.29 (1H, dddm, J=8.8, 7.7, 5.1 Hz), 3.63 (1H, dq, J=9.5, 7.0 Hz), 3.75 (1H, dq, J=9.5, 7.0 Hz), 3.88 (1H, ddd, J=8.4, 3.7, 1.1 Hz), 5.87 (1H, d, J=11.0 Hz), 6.04 (1H, dt, J=8.4, 1.1 Hz), 6.56 (1H, dd, J=8.4, 7.7 Hz), and 7.17 (1H, dd, J=11.0, 8.8 Hz). MS *m/z*: 214 (M$^+$ for ^{37}Cl, 7), 212 (M$^+$ for ^{35}Cl, 26), 177 (54), 160 (30), 141 (30), 131 (72), 103 (26), 91 (22), 77 (35), 72 (100), and 44 (43). IR: 3036, 2972, 2872, 1681, 1380, 1101, 919, and 713 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=226 nm ($\varepsilon$=5500).

20: A colorless oil, 119 mg; 27.9%. Found: C, 61.88; H, 6.30%; M.W., 212.0601 (M$^+$ for ^{35}Cl). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: C, 62.12; H, 6.16%; M.W., 212.0603. ^{1}H NMR δ=1.18 (3H, t, J=7.0 Hz), 1.86 (1H, dddd, J=14.7, 6.2, 2.2, 0.7 Hz), 2.33 (1H, dd, J=14.7, 8.1 Hz), 3.46 (1H, dq, J=9.2, 7.0 Hz), 3.52 (1H, dq, J=9.2, 7.0 Hz), 3.63 (1H, ddm, J=8.4, 7.0 Hz), 3.74 (1H, dd, J=7.7, 6.2 Hz), 4.04 (1H, dt, J=8.1, 2.2 Hz), 6.29 (1H, dd, J=8.1, 7.7 Hz), 6.49 (1H, dd, J=8.1, 7.0 Hz), and 7.25 (1H, d, J=8.4 Hz). MS *m/z*: 214 (M$^+$ for ^{37}Cl, 10), 212 (M$^+$ for ^{35}Cl, 30), 183 (84), 177 (61), 166 (64), 141 (41), 91 (29), 72 (100), and 44 (66). IR: 3052, 2972, 2872, 1686, 1638, 1603, 1373, 1332, 1094, 941, and 732 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=230 nm ($\varepsilon$=3800, sh) and 252 (4800).

21: A colorless oil, 0.2 mg; a trace amount. Found: M.W., 212.0605 (M$^+$). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: 212.0603. ^{1}H NMR δ=1.18 (3H, t, J=7.0 Hz), 1.63 (1H, dt, J=13.5, 4.8 Hz), 2.52 (1H, ddd, J=13.5, 8.3, 2.0 Hz), 3.34 (1H, m), 3.45 (1H, dq, J=9.5, 7.0 Hz), 3.57 (1H, dq, J=9.5, 7.0 Hz), 4.01 (1H, d, J=7.2 Hz), 4.02 (1H, dd, J=8.3, 4.8 Hz), 6.12 (1H, dd, J=8.3, 7.2 Hz), 6.70 (1H, dd, J=8.3, 7.5 Hz), and 7.35 (1H, d, J=9.5 Hz). MS *m/z*: 214 (M$^+$ for ^{37}Cl, 6), 212 (M$^+$ for ^{35}Cl, 18), 177 (34), 166 (22), 141 (22), 77 (22), 72 (100), and 44 (43). IR: 3052, 2972, 2870, 1682, 1634, 1375, 1099, 1071, 959, and 722 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=234 nm ($\varepsilon$=4400) and 264 (2500).

22: A colorless oil, 51 mg; 12.0%. Found: M.W., 212.0602 (M$^+$). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: 212.0603. ^{1}H NMR δ=1.25 (3H, t, J=7.0 Hz), 2.20 (1H, ddd, J=13.2, 8.4, 5.5 Hz), 2.59 (1H, ddd, J=13.2, 9.2, 1.1 Hz), 3.07 (1H, ddm, J=9.2, 8.4 Hz), 3.62 (1H, dq, J=9.5, 7.0 Hz), 3.89 (1H, dq, J=9.5, 7.0 Hz), 5.01 (1H, dd, J=9.5, 3.3 Hz), 5.55 (1H, dd, J=5.5, 1.1 Hz), 6.05 (1H, ddd, J=9.5, 5.9, 2.2 Hz), 6.19 (1H, dd, J=11.7, 5.9 Hz), and 6.33 (1H, d, J=11.7 Hz). ^{13}C NMR δ=15.1, 38.2, 38.9, 64.4, 101.9, 106.9, 124.6, 125.3, 126.6, 129.9, and 148.7. MS *m/z*: 214 (M$^+$ for ^{37}Cl, 23), 212 (M$^+$ for ^{35}Cl, 71), 183 (41), 177 (51), 165 (36), 141 (49), 131 (34), 103 (52), 91 (64), 77 (69), 72 (100), 44 (78), and 26 (48). IR: 3020, 2976, 2876, 1643, 1376, 1343, 1179, 1102, 918, 719, and 619 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=212 nm ($\varepsilon$=16500), 254 (1700), and 306 (3200).

23: A colorless oil, 102 mg; 23.9%. Found: M.W., 212.0604 (M$^+$). Calcd for $C_{11}H_{13}O_2{}^{35}Cl$: 212.0603. ^{1}H NMR δ=0.91 (3H, t, J=7.0 Hz), 1.7—1.9 (2H, m), 2.36 (1H, dtd, J=10.3, 4.4, 1.8 Hz), 3.13 (1H, dq, J=9.5, 7.0 Hz), 3.58 (1H, dq, J=9.5, 7.0 Hz), 5.05 (1H, dd, J=9.2, 4.4 Hz), 5.06 (1H, dd, J=5.1, 2.3 Hz), 5.83 (1H, ddd, J=9.2, 5.5, 1.8 Hz), 6.02 (1H, dd, J=11.4, 5.5 Hz), and 6.48 (1H, d, J=11.4 Hz). ^{13}C NMR δ=15.0, 37.4, 39.2, 64.6, 100.6, 108.1, 125.2, 125.8, 126.5, 130.7, and 147.6. MS *m/z*: 214 (M$^+$ for ^{37}Cl, 22), 212 (M$^+$ for ^{35}Cl, 70), 183 (38), 177 (49), 165 (37), 141 (47), 112 (35), 103 (48), 91 (60), 77 (66), 72 (100), 51 (35), 43 (37), and 26 (47). IR: 3022, 2976, 2880, 1643, 1540, 1444, 1375, 1347, 1185, 1105, 921, 713, and 634 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$=210 nm ($\varepsilon$=13800), 258 (1200), and 307 (2400).

Thermal Cycloaddition Reactions of 2, 9, and 16 with 1 under Ordinary Pressure. a) A toluene solution (4 cm^3) of **1** (590 mg) and **2** (424 mg) was heated in a sealed tube at 100 °C for 100 h. The mixture was chromatographed on a silica-gel column to give a mixture of **3**—**6** (117 mg; 16.5%) and a mixture of **7** and **8** (60 mg; 8.5%) together with the recovered **2** (242 mg; 57%). Further fractionation was carried out by means of high-pressure liquid chromatography; and the results are given in Table 3.

b) A toluene solution (4 cm^3) of **1** (600 mg) and **9** (430 mg) was similarly heated in a sealed tube at 120 °C for 100 h. After silica-gel column chromatography of the mixture, a mixture of adducts (10 mg; 2%) and the recovered **9** (394 mg; 92%) was identified. Further characterization was carried out by high-pressure liquid chromatography.

c) A toluene solution (4 cm^3) of **1** (290 mg) and **16** (141 mg) was similarly heated in a sealed tube at 100 °C for 25 h to achieve ca. 15% conversion. After preliminary separation by silica-gel column chromatography, the mixture was further fractionated through high-pressure liquid chromatography; the product ratio is shown in Table 3.

References

1) G. R. Tian, S. Sugiyama, A. Mori, and H. Takeshita, *Chem. Lett.*, **1987**, 1557; *Bull. Chem. Soc. Jpn.*, **61**, 2393 (1988).

2) M. J. Goldstein and B. G. Odell, *J. Am. Chem. Soc.*, **89**, 6356 (1967).

3) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978); R. van Eldik, T. Asano, and W. J. le Noble, *ibid.*, **89**, 549 (1989).

4) S. Itô, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, **1969**, 1815.

5) The measurement was carried out by a GSX 270 H Model spectrometer with the VCOSYN pulse sequence of the JEOL GSX series software.

6) H. Takeshita, M. Shima, and S. Itô, *Bull. Chem. Soc. Jpn.*, **46**, 2915 (1973).

7) K. Saito, T. Watanabe, and K. Takahashi, *Chem. Lett.*, **1989**, 2099.

8) The results will be published elsewhere.