Novel Preparation of 1- and 3-Substituted Bicyclo[3.2.2]nona-3,6,8-trien-2-ones from Tropones and 2,3-Bis(methoxycarbonyl)-7-oxabicyclo-[2.2.1]heptadiene by High-Pressure Cycloaddition-Thermal Cycloreversion Procedure

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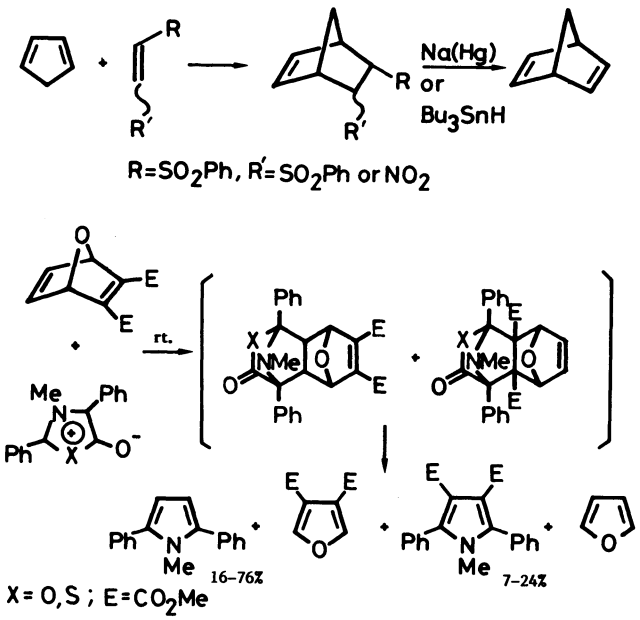
The Diels–Alder adduct of tropone with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene formed homobarrelenone on heating at 130 °C. Similarly prepared were 1-hydroxy-, 3-methoxy-, 1-chloro-, and 3-chlorohomobarrelenones. High-pressure cycloaddition improved the yields of the Diels–Alder adducts. In reactions of 2-methoxy- and 2-chlorotropones with the 7-oxanorbornadiene derivative, the endo-isomers were predominantly produced together with the exo-isomers.

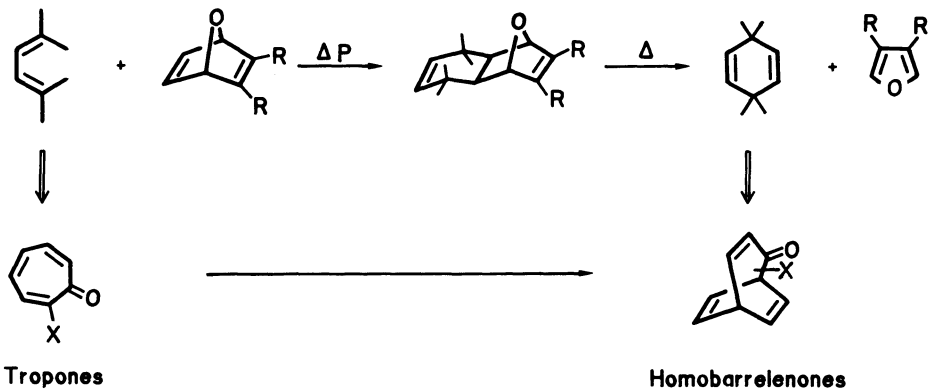
There have been a number of Diels–Alder[1] and retro-Diels–Alder[2] reactions applied to organic syntheses. However, particularly important is the development of a synthon equivalent to acetylene for the cycloaddition reactions, since there seems to still be no versatile procedure; oxidative decarboxylations of Diels–Alder adducts from maleic acid were successful only in limited instances,[3] or reductive eliminations of halogens from dihaloethene adducts sometimes have limitations, depending on the other functional groups in the molecule.[4] A recently developed two-step sequence, Diels–Alder reaction of dienes to 1,2-bis(phenylsulfonyl)ethene[5] and β-nitrosulfonylethene[6] and subsequent reductive elimination with sodium amalgam or tributyltin hydride, usually gave good results; however, the use of mercury would be undesirable from environmental points of view.

Since it is well-known that cycloadducts of furans have a tendency to cyclorevert,[7] 7-oxabicyclo[2.2.1]-heptadiene, which corresponds to the Diels–Alder adduct of furan and acetylene,[8] should serve as a substitute for acetylene.

In fact, the 1,3-dipole additions of 7-oxabicyclo-[2.2.1]heptadiene derivatives and 1,3-dipoles have given five-membered heteroaromatic compounds via



Scheme 1.



Scheme 2.

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the cycloaddition-fragmentation reactions.[9] We herein describe the synthesis of homobarrelenones **3a**,[10] **3b**, **3d**, **4c**, and **4d** by the thermolyzing the Diels–Alder adducts obtained from 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1**)[11] and tropones **2a—d** under high-pressure conditions. To date, only a few derivatives of **3** have been prepared,[12–14] including the 6,7-bis(methoxycarbonyl) derivative by the Diels–Alder addition of **2a** with dimethyl butynedioate.[14,15] Since the derivatives of **3** were recently utilized in natural product syntheses,[12] a versatile synthesis of **3** must be worthwhile.

Results and Discussion

Thermal Reaction of 1 and Tropone. In 1972, Sasaki et al.[16] described the Diels–Alder reaction of tropone **2a** with **1** to form a 1:1-adduct **5a**. However, we have found, through a repeated experiment, a formation of three other products **3a**, **6**, and **7a** together with the expected adduct **5a** even under the Diels–Alder conditions. The ^{1}H NMR data of **3a** were in accord with those reported,[10] and the structures of **6** and **7a** were deduced to be 3,4-bis(methoxycarbonyl)-furan and 1-indanone, respectively, from their NMR data. The reaction also gave better results under high-pressure conditions; at a pressure of 3000 bar, the yield of the Diels–Alder adduct was improved to 88%. Therefore, a retro-Diels–Alder fragmentation of **5a** to **3a** and **6** might be quite facile and the process can be used for the synthesis of derivatives of **3**.

Thermal Reaction of 1 and Tropolone. The reaction of tropolone **2b** with **1** at 130 °C under 1 bar similarly gave, together with the adduct **5b**[16] in 50% yield, fragmentation products 1-hydroxyhomobarrelenone (**3b**), 7-hydroxy-1-indanone (**7b**), and **6**. Again, a reaction under 3000 bar afforded **5b** in 67% yield. The structure of **3b** was confirmed by the NMR data and that of **7b** was identified by a comparison with the authentic sample.[17]

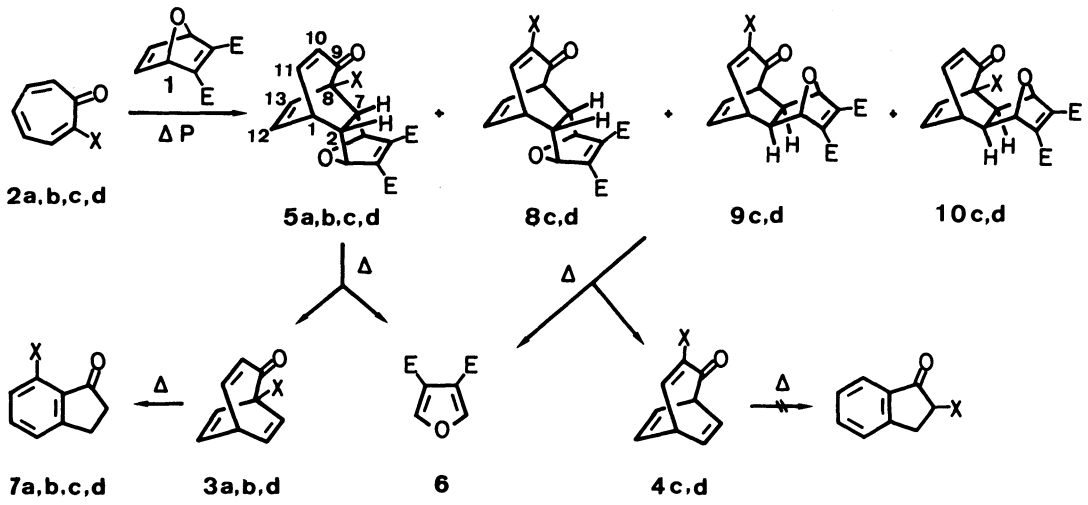
Thermal Reactions of 1 and 2-Methoxy- and 2-Chlorotropones. This high-pressure reaction could be further extended to 2-methoxytropone (**2c**) and 2-chlorotropone (**2d**) with **1**; in both cases, three adducts **5c**, **8c**, and **9c** from **2c** and **5d**, **8d**, and **9d** from **2d** formed under 3000 bar. On the other hand, the reactions at 1 bar with **2c** and **2d** were rather complicated; new types of Diels–Alder adducts **10c** and **10d** were isolated together with the cycloreversed homobarrelenones **3d**, **4c**, and **4d** and indanones **7c** and **7d**. Table 1 summarized the results of Diels–Alder reactions.

The structures of Diels–Alder adducts from **2c** and **2d** were established by the ^{1}H and ^{13}C NMR spectroscopies. The chemical shifts and the coupling constants are summarized in Tables 2 and 3. Since the NMR spectra of the main product **5c** resembled those of **5a** and **5b**, the structure of **5c** was determined to be an endo–exo [4+2]π-adduct[18] with a substituent on the bridge-head carbon.

From the splitting patterns of H_2 and H_7 ($J_{1,2}$=0 Hz and $J_{7,8}$=1.5 Hz) and those of H_3 and H_6 ($J_{2,3}$=$J_{6,7}$=0 Hz), the structure of **8c** was deduced to be another endo–exo [4+2]π-adduct with a chlorine substituent at C-10.

While **9c** also had a substituent on C-10 and the signals of H_3 and H_6 appeared as two singlets, the coupling constants of $J_{1,2}$ (5.5 Hz) and $J_{7,8}$ (5.5 Hz) suggested that H_2 and H_7 had an endo configuration in bicyclo[3.2.2] framework. Therefore, **9c** was the exo–exo [4+2]π-adduct.

The structure of **10c** was the exo–exo [4+2] π-adduct



Scheme 3.

Table 1. Diels–Alder Reactions of **1** and **2**

2	Conditions (°C, h)	Product (Yield/%)[c] 5	8	9	10	3	4	6	7	Endo/Exo	Site selectivity
2a	100, 11[a]	88									
	130, 12[b]	64				11		21	5		
2b	120, 12[a]	67									
	130, 12[b]	50				11		14	2		
2c	120, 12[a]	34	12	4						11.5	2.1[d]
	130, 12[b]	24	11	3.4	2.6		3	16	4	5.8(8.5)[e]	1.6[d]
	130, 20[b]	25					17	26	10		
2d	120, 12[a]	44	20	7				14		9.1	1.6
	130, 20[b]	28	13	5	6	11	6	35	8	3.7(6.9)[e]	2.2[d]

a) Under 3000 bar. b) Under 1 bar. c) Yield was based on consumed **2**. d) These values were ratios including homobarrelenones and indanones. e) These values were ratios adding the yields of **6** to those of endo-adducts.

Table 2. NMR Data of 1:1-Adducts

	5a	**5b**	**5c**	**5d**	**8c**	**8d**	**9c**	**9d**	**10c**	**10d**
R_1	H	OH	OMe	Cl	H	H	H	H	OMe	Cl
R_2	H	H	H	H	OMe	Cl	OMe	Cl	H	H
H-1	3.44	3.61	3.43	3.48	3.5	3.54	3.7	3.7	3.61	3.63
H-2	2.50	2.24	2.64	2.62	2.48	2.52	2.6	2.7	2.60	2.69
H-3	4.92	4.70	4.91	4.96	4.90	4.90	4.86	4.90	4.86	4.90
H-6	5.01	5.52	5.41	5.69	4.98	5.02	4.92	4.95	5.07	5.09
H-7	2.70	2.58	2.64	2.76	2.68	2.74	2.6	2.7	2.72	3.03
H-8	3.68	OH	OMe	Cl	3.8	3.94	3.7	3.98	OMe	Cl
H-10	5.70	5.88	5.74	5.90	OMe	Cl	OMe	Cl	6.05	6.16
H-11	7.18	7.30	7.14	7.26	6.16	7.48	5.81	7.16	6.88	6.92
H-12	6.24	6.32	6.37	6.44	6.51	6.48	6.64	6.64	6.61	6.59
H-13	6.10	5.92	6.06	6.04	6.08	6.16	6.14	6.22	6.27	6.19
C-1	48.2	49.1	47.1	49.8	48.8	47.8	46.9	46.8	44.2	45.6
C-2	39.7	39.7	39.7	38.8	36.7	39.5	35.1	38.0	38.0	37.3
C-3[a]	85.9	83.4	83.5	85.9	85.7	85.6	81.5	81.8	80.1	80.4
C-4[a]	145.7	145.4	145.7	145.6	145.4	145.5	145.4	145.2	144.8	145.3
C-5[a]	146.1	145.8	146.1	146.4	146.3	146.1	145.8	145.8	146.3	145.6
C-6[a]	86.7	85.3	85.9	86.3	86.6	86.7	83.9	83.8	83.2	83.6
C-7	41.8	46.3	45.8	48.9	41.7	41.5	45.4	46.0	52.5	57.4
C-8	57.0	82.1	88.4	81.1	54.9	55.9	55.1	54.9	90.2	80.8
C-9	196.3	195.3	195.1	187.7	191.8	189.0	192.3	189.7	193.2	187.0
C-10	126.8	125.7	128.6	127.7	151.1	132.7	154.9	136.4	132.3	132.8
C-11	153.7	155.8	152.8	153.8	120.8	150.0	114.0	144.1	146.4	146.8
C-12	136.1	133.8	133.5	135.0	137.6	136.1	141.0	139.6	138.2	138.3
C-13	129.5	132.6	130.3	132.5	126.2	127.0	129.0	129.9	133.5	136.3

a) Assignments of C-3, C-6, C-4, and C-5 could be reversed.

Table 3. Coupling Parameters (Hz) of 1:1-Adducts

	5a	**5b**	**5c**	**5d**	**8c**	**8d**	**9c**	**9d**	**10c**	**10d**
$J_{1,2}$	0	0	0	1	—	—	5.5	5.5	5.9	5.9
$J_{1,10}$	2	0	1	0.7	—	—	×	×	0.7	0.7
$J_{1,11}$	8	8	8.5	8	9.5	9	9.5	9	8.8	8.8
$J_{1,12}$	8	7	7	7.5	7.5	7.5	7	7	7.0	7.3
$J_{2,3}$	1	0	1.5	1.5	0	0	0	1	1.1	1.1
$J_{2,7}$	8	8	—	7.5	8	8	8.5	8	8.8	8.8
$J_{6,7}$	1	0	1.5	1.5	0	0	0	1	1.1	1.1
$J_{7,8}$	0	×	×	×	1.5	1.5	5.5	3.5	×	×
$J_{8,13}$	8	×	×	×	7.5	7.5	7.5	7	×	×
$J_{10,11}$	11	11	11	11	×	×	×	×	11.0	11.0
$J_{12,13}$	8	8	9	9	7.5	7.5	8	8.5	8.8	8.8

—: Not observed. ×: Not existed.

from the presence of four olefinic protons and the value of the coupling constant ($J_{1,2}$=5.9 Hz, $J_{2,3}$=$J_{6,7}$= 1.1 Hz). Similarly, the structures of four 1:1-adducts **5d**, **8d**, **9d**, and **10d** from **1** and **2d** were confirmed from the NMR data, as shown in Scheme 3.

In addition, the structures of homobarrelenones **3d**, **4c**, and **4d** were also clarified by their NMR analysis. All ^{13}C NMR displayed seven lines. Since the ^{1}H NMR spectrum of **3d** showed six olefinic protons, **3d** was deduced to be 1-chlorohomobarrelenone. In **4c** and **4d**, the appearance of five olefinic and two methine protons determined the structures to be 3-methoxy- and 3-chlorohomobarrelenones, respectively.

The indanone **7c** was identified to be 7-methoxy-1-indanone by a direct comparison with the authentic sample.[17]

Pressure Effect on the Cycloaddition Reaction. Table 1 shows the pressure effect on the endo/exo ratio and the site selectivity [(**5**+**10**):(**8**+**9**)] in the reactions between **1** and **2c** or **2d**. In both cases, the pressure did not affect to the site selectivity under 3000 bar, but the endo/exo ratio was larger as roughly twice than that under 1 bar. When the time-course of the cycloreversion of the endo-adduct **5d** and exo-adduct **10d** in toluene-d_8 was monitored by ^{1}H NMR spectroscopy, the formation of **6** was observed in ca. 40% conversion from **5d** and in less than 1% conversion from **10d** after heating at 130 °C for 24 h. Therefore, an endo/exo ratio under 1 bar could be estimated to be larger than the observed value (5.8 for **2c** and 3.7 for **2d**). If all of **6** was formed by the cycloreversion of endo-adducts and the yields of **6** were added to the yields of endo-adducts, the endo/exo ratios became 8.5 and 6.9 in the reactions between **1** and **2c** or **2d**, respectively. This means that the change of the endo/exo ratio was insignificant within the present pressure range.

Thermal Cycloreversion of Adducts. To obtain homobarreleones, the adducts were thermolyzed at 130 °C for a prolonged period; e.g., **5a** gave **3a**, **7a**, and **6** in 26, 22, and 48% yields, respectively. The results are summarized in Table 4. The isolated yields for **3** and **4** were relatively low. This was due to their volatility and a facile isomerization to indanone derivatives. Therefore, in order to avoid any further transformation of **3** to **7**, we thermolyzed **5** in a flow system and could improve the yield of **3a** to 64% without indanone formation. This was applicable to preparing other homobarrelenones **3b** and **3d**.

Table 4. Pyrolysis of Adducts

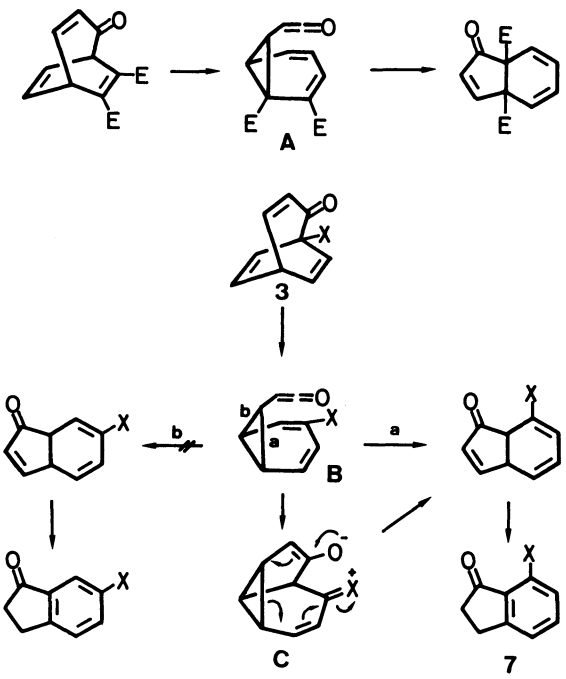
Adducts	Condition		Product (Yield/%)[a]		
5a	130°C,	15 h	**3a** (26)	**7a** (22)	**6** (48)
5b	120°C,	6d	**3b** (39)	**7b** (36)	**6** (81)
5c	120°C,	7d		**7c** (95)	**6** (100)
8c+**9c**	130°C,	7d	**4c** (50)		**6** (50)
5d	130°C,	12 h	**3d** (17)	**7d** (17)	**6** (62)
8d+**9d**	130°C,	6d	**4d** (86)		**6** (88)

a) Yield was based on comsumed adduct.

An attempted fragmentation of **5c**, the major product from **2c**, resulted only the formation of **7c**; however **5d**, the major adduct from **2d**, produced **3d** and 7-chloro-1-indanone (**7d**).[19] Thus, the electron-releasing group on the bridge-head carbon facilitates the indanone formation.

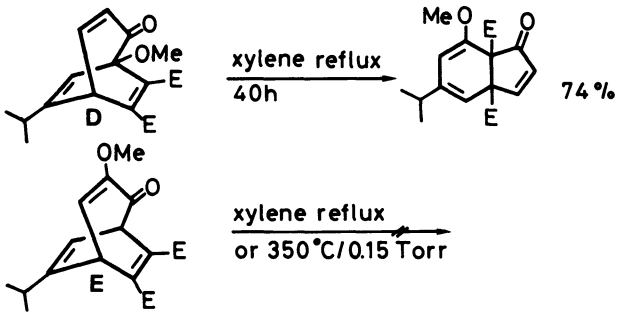
Mechanism of Thermal Rearrangement. The mechanism of thermal isomerization, homobarrelenones to dihydroindenones, has already been proposed;[15] a [3,3] sigmatropic shift of a homobarrelenone to the 7-*syn*-norcaradienylketene intermediate (**A**) followed by a [3,5] sigmatropic shift (antarafacial or Möbius) to a dihydroindenone. If an intermediate (**B**) like **A** was involved, there should be two routes (a and b) to indanones. However, an exclusive formation of 7-substituted indanones is consistent only with path a from **B**, as illustrated in Scheme 4. The methoxyl group of 1-methoxyhomobarrelenone would assist the formation of the tricyclic intermediate (**C**) and the bond a cleavage to 7-methoxyindanone. Such an intermediate **C** has been noticed in the photochemical isomerization of 5-hydroxytricyclo[3.3.2.0^{2,4}]deca-7,9-dien-6-one[20] and 5-alkyl-1-hydroxy-8-oxabicyclo[3.2.1]-octa-3,6-dien-2-ones.[21]

The by-products **8c** and **9c** from **2c** and **8d** and **9d** from **2d** were, respectively, converted to **4c** and **4d** by cycloreversion. However, **4c** and **4d** gave no indanones, unlike 1-substituted homobarrelenones. A simi-

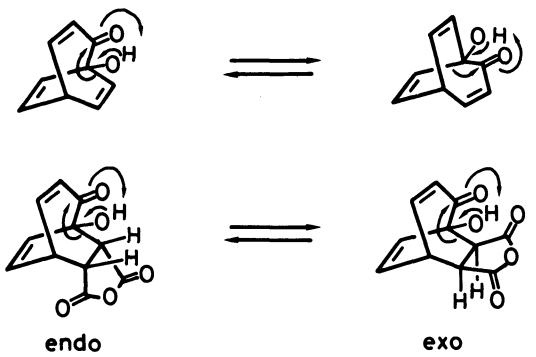


Scheme 4.

lar result has been observed in the pyrolysis of 9-isopropyl-1-methoxy-6,7-bis(methoxycarbonyl)bicyclo-[3.2.2]hepta-3,6,8-trien-2-one (**D**) and 9-isopropyl-3-methoxy-6,7-bis(methoxycarbonyl)bicyclo[3.2.2]hepta-3,6,8-trien-2-one (**E**); **D** gave a dihydroindenone derivative in 74% yield, while **E** did not give any products.[13] Probably, the electron-releasing methoxyl group at the α-position rather increased the electron density of the α,β-unsaturated ketone moiety. No occurrence of an indanone from **4d** could also be explained by the mesomeric effect of the chlorine atom on the α-position of the enone.



Scheme 5.



Scheme 6.

It is interesting that 1-hydroxyhomobarrelenone (**3b**) could be isolated after the thermal reactions, as shown in Table 1; probably, this would be attributable to a suppression of the rearrangement to indanone due to an alternative rearrangement, thermal acyloin rearrangement, which has been detected in the Diels–Alder adducts of maleic anhydride with tropolones.[22]

The NMR Spectral Analysis of Homobarrelenones. The ^{1}H and ^{13}C NMR chemical shifts of homobarrelenones prepared were systematically analyzed. As compiled in Table 5, the ^{13}C NMR chemical shifts of C-7(8) in **3b** and **3d** were at lower fields by ca. 6 ppm than the corresponding carbon in **3a**. Similar low-field shifts were observed for C-13 in 1:1-adducts summarized in Table 2. The chemical shift of the carbonyl carbon in **3a** was 189.7 ppm and the hydroxyl group at C-1 and the methoxyl group at C-3 did not affect the chemical shift of the carbonyl carbons, while the chlorine atom at C-1 and C-3 made the chemical shift of the carbonyl carbon higher by 6—8 ppm. These high field shifts can be explained in terms of the supressed polarization of the carbonyl group due to the polar substituent, the chlorine atom, at the α-position. Similar high field shifts were also observed in other 1:1-adducts (Table 2).

In the ^{1}H NMR spectra, protons H_3 in **3b** and **3d** and H_1 in **4c** and **4d** appeared at lower fields by ca. 0.3—0.4 ppm than those in **3a**. Protons H_8 and H_{10} in **8** and **5** behaved similarly. Thus, the substituent, being across the carbonyl group, caused a considerable change in the proton chemical shift.

Conclusion

As mentioned above, the Diels–Alder and the retro-Diels–Alder reactions provided a versatile two-step synthesis of structurally interesting bicyclic ketones, homobarrelenones. Substituted homobarrelenones at

Table 5. NMR Data of Homobarrelenones

	3a	3b	3d	4c	4d
R_1	H	OH	Cl	H	H
R_2	H	H	H	OMe	Cl
H-1	4.15	OH	Cl	4.38(0.23)	4.52(0.37)[a]
H-3	5.04	5.42(0.38)	5.34(0.30)	OMe	Cl
H-4	7.02	7.22(0.20)	7.14(0.12)	6.16(−0.96)	7.36(0.34)
H-5	3.85	4.04(0.19)	3.90(0.05)	3.96(0.11)	4.02(0.17)
H-6,9	6.67	6.66(−0.01)	6.76(0.09)	6.82(0.15)	6.82(0.15)
H-7,8	6.33	6.28(−0.05)	6.34(0.01)	6.42(0.09)	6.48(0.15)
C-1	59.4	86.0(26.6)	77.3(17.9)	54.5(−4.9)	58.4(−1.0)
C-2	189.7	189.9(0.2)	181.5(−8.2)	187.1(−2.6)	183.9(−5.8)
C-3	124.9	121.9(−3.0)	123.5(−1.4)	146.1(21.2)	127.3(2.4)
C-4	153.2	155.2(2.0)	153.4(0.2)	120.1(−33.1)	149.6(−3.6)
C-5	41.5	41.9(0.4)	40.2(−1.3)	38.3(−3.2)	41.2(−0.3)
C-6,9	138.5	137.7(−0.8)	136.0(−2.5)	140.2(1.7)	138.7(0.2)
C-7,8	128.9	134.4(5.5)	135.2(6.3)	128.7(−0.2)	129.1(0.2)

a) Figures shown in the parentheses were chemical shift differences with unsubstituted **3a**.

the bridge-head carbon tended to rearrange to the indanones, while 3-isomers did not.

This procedure, high-pressure cycloaddition and thermal fragmentation, may be widely applicable, and **1** will conveniently serve as a substitute for acetylene.

Experimental

The elemental analyses were performed by Miss S. Hirashima of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured using a JEOL 100 and 270H spectrometer in $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in the unit δ. Mass spectra were measured with a JEOL OISG-2 spectrometer. IR spectra were taken as a $CHCl_3$ solution using a Jasco IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer.

Preparation of 1 under 3000 bar. An ether solution (12 cm³) of furan (13.1 g) and dimethyl butynedioate (5.80 g) was kept at room temperature under 3000 bar for 20 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **1** [colorless oil, 5.53 g, 66%] together with two 1:1-adducts [4.31 g, 34%] between **1** and furan.

Thermal Reaction of 2a and 1. a) A chlorobenzene (CB) solution (1.5 cm³) of **2a** (109 mg) and **1** (267 mg) was heated at 100 °C under 3000 bar for 11 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **5a** [colorless crystals, mp 100—102 °C, (lit,[16] 100—102 °C), 271 mg, 88%. ^{1}H NMR δ=2.50 (1H, d, J=8 Hz), 2.70 (1H, d, J=8 Hz), 3.44 (1H, tm,J=8 Hz), 3.68 (1H, d, J=8 Hz), 3.78 (3H, s), 3.80 (3H, s), 4.92 (1H, d, J=1 Hz), 5.01 (1H, d, J=1 Hz), 5.70 (1H, dd, J=11, 2 Hz), 6.10 (1H, t, J=8 Hz), 6.24 (1H, t, J=8 Hz), and 7.18 (1H, dd, J=11, 8 Hz)] and recovered **1** [61.4 mg].

b) A CB solution (3 cm³) of **2a** (303 mg) and **1**(611 mg) was heated at 130 °C for 12 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **3a** [colorless needles, mp 45 °C (lit,[10] 44 °C), 44.6 mg, 11%. ^{1}H NMR δ=3.85 (1H, m), 4.15 (1H, tq, J=6.5, 1.5 Hz), 5.04 (1H, ddd, J=11, 2, 1 Hz), 6.33 (2H, ddd, J=8, 6.5, 1.5 Hz), 6.67 (2H, ddd, J=8, 6.5, 1.5 Hz), and 7.02 (1H, dd, J=11, 8 Hz)], **5a** [582 mg, 64%], **6** [110 mg, 21%], and **7a** [a colorless oil, 21 mg, 5%. ^{1}H NMR δ=2.6—2.8 (2H, m), 3.0—3.2 (2H, m), and 7.3—7.8 (4H, m)].

Thermal Reaction of 2b and 1. a) A CB solution (2 cm³) of **2b** (244 mg) and **1** (426 mg) was heated at 120 °C under 3000 bar for 12 h. The mixture gave **5b** [mp 114—115 °C, (lit,[16] 114—115 °C), 394 mg, 67%], recovered **2b** [28 mg], and **1** [22.4 mg].

b) A CB solution (1 cm³) of **2b** (122 mg) and **1** (210 mg) was heated at 130 °C for 12 h. The mixture gave **3b** [a colorless oil, 14.3 mg, 11%. Found: m/z, 148.0523 (M⁺). Calcd for $C_9H_8O_2$: 148.0523. IR ν: 3450 and 1670 cm⁻¹. UV λ_{max}^{MeOH}: 202 nm (ε=11700), 229 (3500), and 282 (540)], **5b** [165 mg, 50%], **6** [25.4 mg, 14%], and **7b** [colorless crystals, mp 111—112 °C (lit,[17] 111 °C), 3 mg, 2%. ^{1}H NMR δ=2.7—2.8 (2H, m), 3.0—3.2 (2H, m), 6.71 (1H, d, J=7.5 Hz), 6.89 (1H, d, J=7.5 Hz), 7.43 (1H, t, J=7.5 Hz), and 9.02 (1H, s). UV λ_{max}^{MeOH}: 221 nm (ε=21750), 255 (10600), and 314 (3400)].

Thermal Reaction of 2c and 1. a) A CB solution (2 cm³) of **2c** (358 mg) and **1** (680 mg) was heated at 120 °C under 3000 bar for 12 h. The mixture gave **5c** [colorless crystals, mp 102—103 °C, 306 mg, 34%. Found: C, 62.20; H, 5.23%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%. IR ν: 1720 cm⁻¹. UV λ_{max}^{MeOH}: 221 nm (ε=12100)], **8c** [colorless crystals, mp 129—131 °C, 99 mg, 12%. Found: C, 62.29; H, 5.21%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%. IR ν: 1730, 1710, and 1675 cm⁻¹. UV λ_{max}^{MeOH}: 234 nm (ε=9000) and 287 (2700)], and **9c** [colorless crystals, mp 176.5—178 °C, 33 mg, 4%. Found: C, 62.39; H, 5.22%. Calcd for $C_{18}H_{18}O_7$: C; 62.42; H, 5.24%. IR ν: 1775 cm⁻¹. UV λ_{max}^{MeOH}: 232 nm (ε=6600) and 292 (2050)].

b) A CB solution (1 cm³) of **2c** (126 mg) and **1** (214 mg) was heated at 130 °C for 12 h to give **4c** [a colorless oil, 4.1 mg, 3%. Found: m/z, 162.0682 (M⁺). Calcd for $C_{10}H_{10}O_2$: 162.0681. IR ν: 1720, 1680, 1640, 1605, and 1120 cm⁻¹. UV λ_{max}^{MeOH}: 201 nm (ε=9150), 239 (2600), and 305 (990)], **5c** [76.6 mg, 24%], **6** [27.3 mg, 16%], **7c** [colorless plates, mp 98.5—100 °C (lit,[17] 102—103 °C), 6 mg, 4%. ^{1}H NMR δ=2.6—2.75 (2H, m), 3.0—3.15 (2H, m), 4.90 (3H, s), 6.76 (1H, d, J=7.5 Hz), 6.96 (1H, d, J=7.5 Hz), and 7.50 (1H, t, J=7.5 Hz)], **8c** [36 mg, 11%], **9c** [11 mg, 3.4%], and **10c** [colorless crystals, mp 142—143 °C, 9.1 mg, 2.4%. Found: C, 62.37; H, 5.21%. Calcd for $C_{18}H_{18}O_7$: C, 62.42: H, 5.24%. IR ν: 1725, 1675, and 1230 cm⁻¹. UV λ_{max}^{MeOH}: 220 nm (ε=9500) and 289 (1250)].

c) A CB solution (2 cm³) of **2c** (273 mg) and **1** (448 mg) was heated at 130 °C for 20 h to give **4c** [54.8 mg, 17%], **6** [96 mg, 26%], **5c** [170 mg, 25%], and **7c** [34 mg, 10%].

Thermal Reaction of 2d and 1. a) A CB solution (2 cm³) of **2d** (281 mg) and **1** (420 mg) was heated at 120 °C under 3000 bar for 12 h. The mixture gave **5d** [colorless needles, mp 146—147 °C, 231 mg, 44%. Found: C, 58.10; H, 4.32%. Calcd for $C_{17}H_{15}O_6Cl$: C, 58.21; H, 4.31%. IR ν: 1740, 1720, 1685, 1640, and 1225 cm⁻¹. UV λ_{max}^{MeOH}: 227 nm (ε=11000)], **8d** [colorless needles, mp 122—123 °C, 106.5 mg, 20%. Found: C, 58.23; H, 4.31%. Calcd for $C_{17}H_{15}O_6Cl$: C, 58.21; H, 4.31%. IR ν: 1730, 1715, and 1680 cm⁻¹. UV λ_{max}^{MeOH}: 234 nm (ε=9700)], **9d** [colorless needles, mp 157—159 °C, 37.3 mg, 7%. Found: C, 58.10; H, 4.33%. Calcd for $C_{17}H_{15}O_6Cl$: C, 58.21; H, 4.31%. IR ν: 1720 and 1670 cm⁻¹. UV λ_{max}^{MeOH}: 224 nm (ε=7800) and 268 (3400)], **6** [38.8 mg, 14%], and unreacted **2d** [70.3 mg].

b) A CB solution (5 cm³) of **2d** (234 mg) and **1** (350 mg) was heated for 130 °C for 12 h to give **3d** [colorless needles, mp 67—69 °C, 14 mg, 6%. Found: m/z, 166.0160 and 168.0154 (M⁺). Calcd for C_9H_7OCl: 166.0183 and 168.0154. IR ν: 1680 cm⁻¹. UV λ_{max}^{MeOH}: 203 nm (ε=12800), 227 (3250), and 283 (700)], **4d** [colorless needles, mp 85.5—87 °C, 23.5 mg, 11%. Found: m/z, 166.0179 and 168.0146 (M⁺). Calcd for C_9H_7OCl: 166.0183 and 168.0154. IR ν: 1680 and 1630 cm⁻¹. UV λ_{max}^{MeOH}: 203 nm (ε=9800), 241 (3600), and 295 (900)], **5d** [128.5 mg, 28%], **8d** [61 mg, 13%], **9d** [24 mg, 5%], **10d** [colorless needles, mp 152—153 °C, 27.5 mg, 6%. Found: C, 58.32; H, 4.27%. Calcd for $C_{17}H_{15}O_6Cl$: C, 58.21; H, 4.31%. IR ν: 1730 cm⁻¹. UV λ_{max}^{MeOH}: 224 nm (ε=7600)], **6** [84 mg, 35%], **7d** [colorless needles, mp 92—93.5 °C (lit,[19] 95 °C), 17.3 mg, 8%. ^{1}H NMR δ=2.6—2.9 (2H, m), 3.0—3.3 (2H, m), and 7.2—7.5 (3H, m)], and unreacted **2d** [52 mg].

Thermal Reaction of 5a. a) A CB solution (1.5 cm³) of **5a** (254 mg) was heated at 130 °C for 15 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **3a** [5 mg, 25%], **6** [13 mg, 48%], **7a** [4.3 mg, 22%], and **5a** [208 mg].

b) Crystalline **5a** (130 mg) was placed in a tube equipped with a dry-ice cold finger and thermolyzed at 160—170 °C for 2 h under 50 mmHg (1 mmHg=133.322 Pa). The thermolysate deposited on a wall was washed with ether and chromatographed on a PTLC to give **3a** [28.9 mg, 64%] and **6** [45.2 mg, 70%]. 21 mg of **5a** was remained in a tube.

Thermal Reaction of 5b. a) A CB solution (1 cm^3) of **5b** (175.5 mg) was heated at 120 °C for 6 d to give **3b** [17.4 mg, 39%], **6** [45 mg, 81%], **7b** [16 mg, 36%], and **5b** [75.5 mg].

b) Crystalline **5b** (160 mg) was thermolyzed at 180—185 °C for 2 h under 50 mmHg to give **3b** [42 mg, 59%], **6** [60 mg, 68%], and **7b** [18 mg, 25%].

Thermal Reaction of 5c. A CB solution (1 cm^3) of **5c** (132 mg) was heated at 120 °C for 7 d to give **7c** [40 mg, 95%], **6** [48 mg, 100%], and **5c** [42 mg].

Thermal Reaction of a Mixture of 8c and 9c. A xylene (XL) solution (1 cm^3) of a 3:1-mixture of **8c** and **9c** (105 mg) was heated at 130 °C for 7 d to give **4c** [14.7 mg, 50%], **6** [18.4 mg, 50%], and a mixture of **8c** and **9c** [35 mg].

Thermal Reaction of 5d. a) A XL solution (1 cm^3) of **5d** (141 mg) was heated at 130 °C for 12 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **3d** [6 mg, 17%], **6** [24.8 mg, 62%], **7d** [6 mg, 17%], and **5d** [65.5 mg].

b) Crystalline **5d** (108 mg) was heated at 180—190 °C for 1.5 h under 50 mmHg to gvie **3d** [21.3 mg, 44%], **6** [37 mg, 62%], and **7d** [17.5 mg, 36%].

Thermal Reaction of a Mixture of 8d and 9d. A XL solution (1 cm^3) of a 2.6:1-mixture of **8d** and **9d** (98 mg) was heated at 130 °C for 6 d to give **4d** [31 mg, 86%], **6** [35 mg, 88%], and unreacted **8d** and **9d** [22 mg].

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