# The High-Pressure Cycloadditions of Tropone to Styrenes. Predominant Formation of [8+2] Cycloadducts from $\alpha$-Methylstyrene

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# The High-Pressure Cycloadditions of Tropone
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# [8+2] Cycloadducts from α-Methylstyrene[1]

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Abstract: High-pressure cycloaddition reactions of tropone to sty-
rene up to 140 °C under various pressures proceeded to give, despite two
products were identified previously, four Diels-Alder adducts, among
which, the 9-phenylbicyclo[3.2.2]nona-3,6-dien-2-ones were predomi-
nant over 8-phenyl derivatives. On the other hand, the reaction with α-
methylstyrene gave three Diels-Alder adducts and two [8+2] cycload-
ducts, but a noticeable feature was a predominance of the latter.

Although Kitahara already explored Diels-Alder reaction of tropone (1) with styrene (2) to furnish an epimeric pair of products,[2] we are interested to extend the high-pressure cycloaddition of 1[3] with 2 and α-methylstyrene (3). Formation of four Diels-Alder adducts from 2 and three Diels-Alder adducts, along with two [8+2] cycloadducts from 3, will be described herein.

## Results and Discussion

**Thermal High-Pressure Cycloaddition.** When tropone (1) and 2 were heated at 140 °C under 5000 bar (1 bar = $10^5$ Pa) for 24 h, 96% of 1 was consumed to give four Diels-Alder adducts (4, 5, 6, and 7).

Since there were all of four possible [4+2] isomers, their structures deduced by the ^{1}H NMR spectral analysis left no ambiguity; although the anisotropic effect from the phenyl group was rather difficult to apply to the structure elucidations due to complicated chemical shift changes of the vinyl protons, spin-coupling patterns of bridge-head methine protons were informative to deduce the orientations and locations of the phenyl group (i.e., 4, 5, 6, and 7 are 9α-, 9β-, 8α-, and 8β-phenylbicyclo[3.2.2]nona-3,6-dien-2-ones (8,9-dihydro-homobarrelenones)). Beside this, the ^{13}C NMR chemical shift comparisons with unsubstituted dihydrohomobarrelenone (8)[2,4] provided unambiguous evidence to elucidate the structures as in cases of the ethoxy and the cyano derivatives.[5,6]

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4: R=H
9: R=Me

5: R=H
10: R=Me

6: R=H
11: R=Me

7

12

13

8
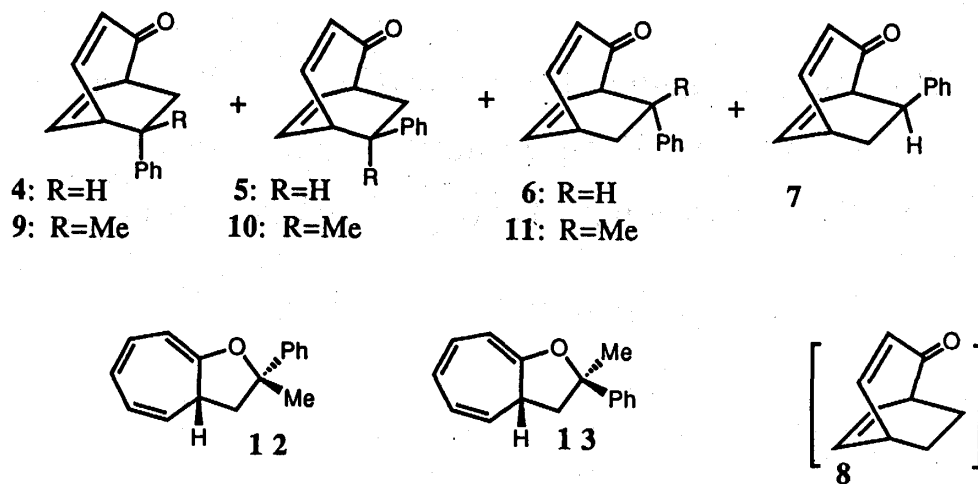
**Scheme 1**

From the results, a similarity of the product distributions of reactions with other dienophiles was noticed; major products were 9-phenyl derivatives (4 and 5) which were identical with authentic samples.[2] It is, therefore, desirable to check the product distributions under various pressures. The results, thus obtained from 150 bar to 10000 bar, are summarized in Table 1.

Throughout the experiments, 4 and 5 were the predominant products, but the ratio of *endo*- to *exo*-adducts was affected by the pressure. While the yields of 8α-(6), 8β-(7), and 9α-(4) derivatives were increased with increasing the pressure, 9β-derivative (5) showed a

**Table 1.** Product Distributions of the Diels-Alder Reactions of 1 to 2 under Various Pressures at 100 °C[a]

| Pressure/bar | Conv./% | *endo*-Adducts | | *exo*-Adducts | | *endo*/*exo* |
| | | 8α-Ph | 9α-Ph | 8β-Ph | 9β-Ph | |
|---|---|---|---|---|---|---|
| 150 | 37 | 4 | 50 | trace | 46 | 1.17 |
| 600 | 56 | 7 | 57 | 4 | 32 | 1.78 |
| 1000 | 66 | 6 | 60 | 3 | 31 | 1.94 |
| 5000 | 87 | 8 | 57 | 7 | 28 | 1.87 |
| 10000 | 78 | 9 | 58 | 8 | 26 | 2.03 |
| 10000[b] | 13 | 6 | 72 | 3 | 19 | 3.55 |

a) Ratios were determined by the ¹H NMR spectrometry.
b) at 20 °C for 124 h.

**Table 2.** Product Distributions of the Diels-Alder Reactions of 1 to 3 under Various Pressures at 100 °C for 12 h[a]

| Pressure/bar | [4+2]-Adducts | | | [8+2]-Adducts | | Reaction |
| | 9α-Ph | 9β-Ph | 8α-Ph | *exo*- | *endo*- | time/h |
|---|---|---|---|---|---|---|
| 3000 | 25 | 21 | 4 | 42 | 8 | 8 |
| 5000 | 24 | 22 | 4 | 41 | 9 | 8 |
| 8000 | 21 | 21 | 6 | 43 | 9 | 7 |
| 10000 | 21 | 22 | 7 | 41 | 9 | 5 |

a) Ratios were determined by the ¹H NMR spectrometry.

sharp decrease of the yields. This is due to the control of the reaction by two independent factors. One is the kinetic control with orbital overlapping to favor the *endo*-adduct formation as the high-pressure conditions greatly suppress the cycloreversion process. Consequently, in the most of the cases, a predominant formation of kinetically controlled products occurs. However, in the cases of tropones, which are capable of forming more than one kinetically-controlled product, other factors, i.e., the volume profile and the steric effect, should be taken into account. In general, the activation volume is known to be pressure-dependent; the larger the steric hindrance, the larger the negative figures for activation volume.[7] And, the first factor favors, under high-pressure conditions, $8\alpha$- and $9\alpha$-adducts (**4** and **6**) over $8\beta$- and $9\beta$-adducts (**5** and **7**), and the second factor favors $9\alpha$- and $9\beta$-adducts (**6** and **7**) over $8\alpha$- and $8\beta$-adducts (**4** and **5**). As the result, the formation of **5** was disfavored. For a closely related phenomenon, formation of $8\beta$-cyano derivative from **1** and acrylonitrile was shown to be temperature dependent as a result of the suppression of the thermodynamically-controlled process under high pressures.[6, 8]

Similarly, the reaction of **1** with $\alpha$-methylstyrene (**3**) at 100 °C under 8000 bar afforded three Diels-Alder products (**9, 10,** and **11**) and two [8+2] cycloadducts (**12** and **13**). Product distributions up to 10000 bar are shown in Table 2. Again, the $^1$H NMR spectra of **9, 10,** and **11,** the Diels-Alder adducts, indicated the type of compounds, but the chemical shift comparisons with those Diels-Alder adducts, **4, 5,** and **6,** from **2** were not so easy, and the nuclear Overhauser effect (NOE) measurements were employed to deduce the structures; e.g., in **9,** C-4 and C-5 protons revealed clear NOE with the methyl signal at $\delta=1.53$ and in **10,** C-5 and C-6 protons did with the methyl signal at $\delta=1.38$. Similarly, with **11,** an irradiation with the frequency of the methyl signal, $\delta=1.54$, caused an enhancement of signals ascribable to C-1 and C-3 protons. Therefore, the orientations of the phenyl group of **9, 10,** and **11** were deduced to be $9\alpha$, $9\beta$, and $8\alpha$ (Fig. 1). The $^{13}$C NMR chemical shift comparisons provided a further supporting evidence.[9] Again, a predominant formation of 9-substituted derivatives was confirmed.

The structures of [8+2] cycloadducts (**12** and **13**) were also deduced on the basis of the NOE by irradiations with frequencies of methyl signals; i.e., in **12,** there was a clear NOE between the methyl and the proton at the ring juncture, C-3a, and in **13,** one of the methylene protons revealed an NOE but not the methine proton at the ring juncture. Therefore, structures of **12** and **13** were elucidated to be *endo*- and *exo*-[8+2] cycloadducts as depicted in Scheme 1.

It is reasonable that preferential formation of [8+2] cycloadducts in the case of **3** is due to an increased electron-donating ability of the polarized, unsymmetrically substituted double bond. This is in accord both with empirical observations from several dienophiles, such as ethoxyethene[5] and diethoxyethene[10] and also with a prediction from the MO point
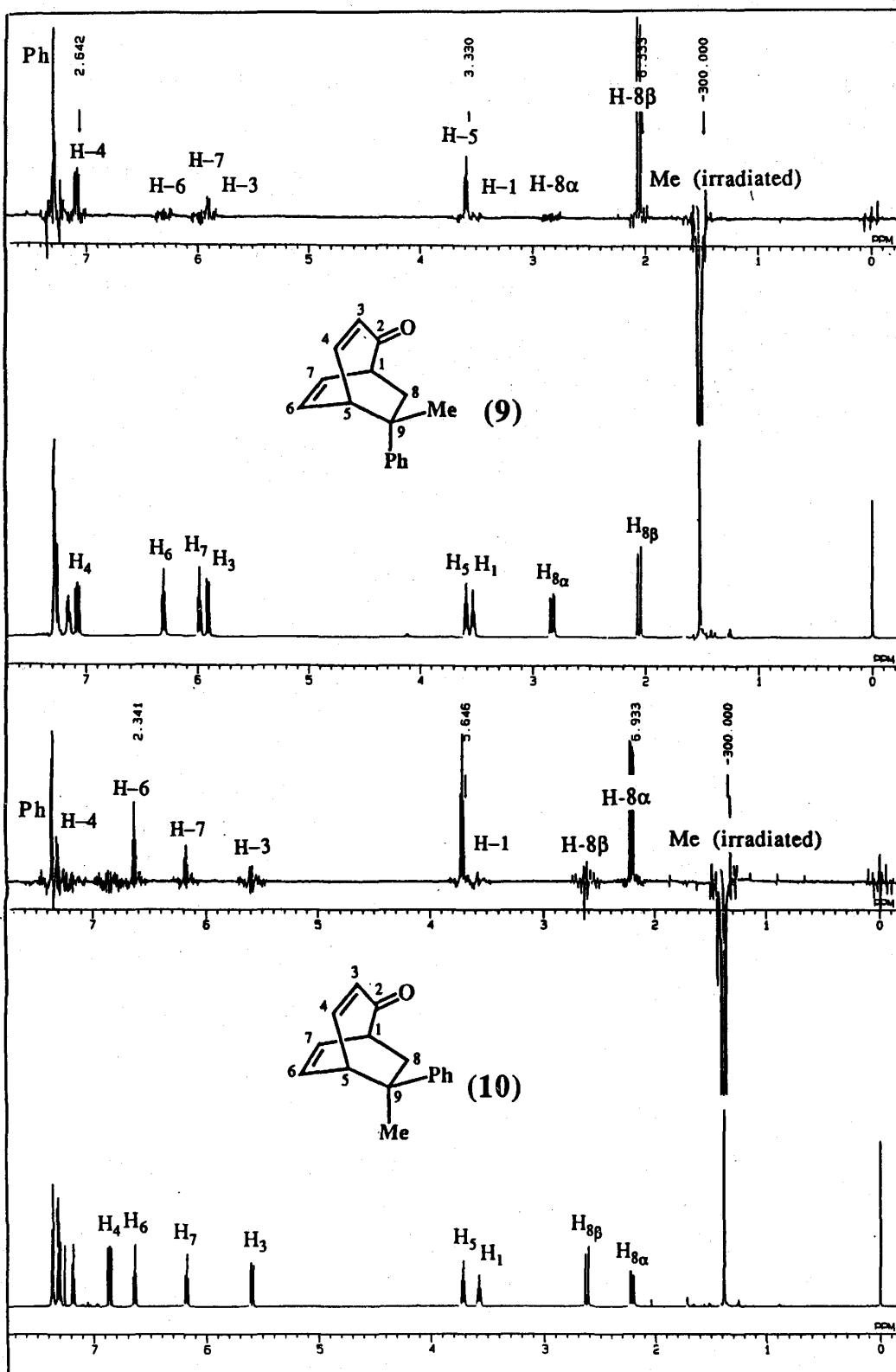
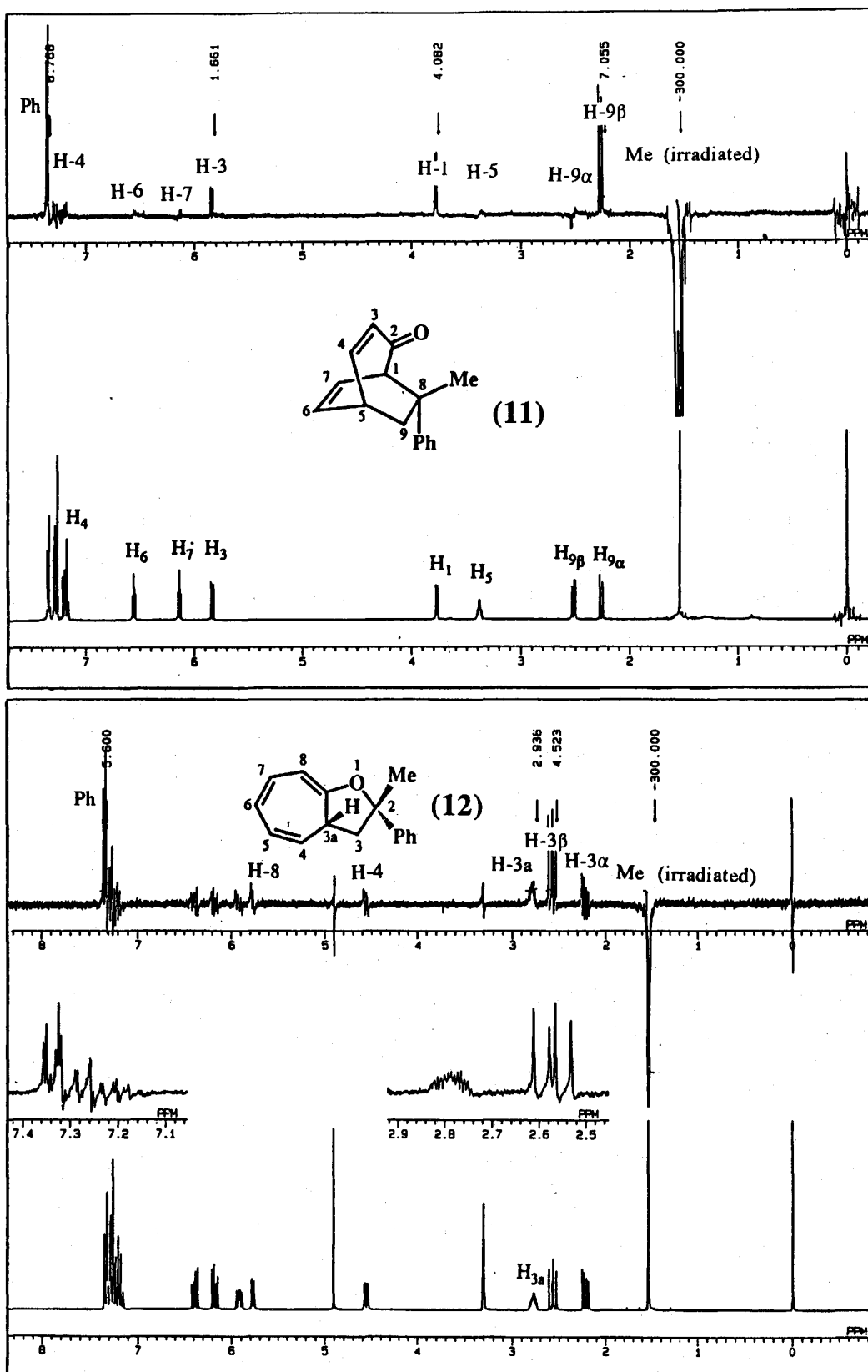**Fig. 1.** The NOE Experimental Data of **9, 10, 11,** and **12.**

Fig. 1. Continued

**Table 3.** The *peri*-Selectivity of the Diels-Alder Reactions of **1** to **3** under Various Pressures at 140 °C for 12 h[a]

| Pressure/bar | Conv./% | Adducts | | Ratio | Reaction |
| --- | --- | --- | --- | --- | --- |
| | | [4+2]- | [8+2]- | [8+2]/[4+2] | time/h |
| 1 | 3 | 42.9 | 57.1 | 1.33 | 95 |
| 3000 | 12 | 42.7 | 57.3 | 1.34 | 8 |
| 5000 | 16 | 41.7 | 58.3 | 1.40 | 8 |
| 8000 | 34 | 47.4 | 52.6 | 1.11 | 7 |
| 10000 | 59 | 49.5 | 50.5 | 1.02 | 5 |

a) Ratios were determined by the ^{1}H NMR spectrometry.

of view. The regioselectivity of thermal [8+2] cycloadditions between **1** and ethenes was explained in terms of an interaction of the LUMO of **1** and HOMO of ethenes.[11] It is known that conjugated substituents of ethenes increase the relative magnitude of the coefficient of the unsubstituted terminus in both frontier orbitals and alkyl groups also increase the remote coefficient in the HOMO.[12] Therefore, the HOMO coefficient of the substituted terminus of **3** becomes larger than that of **2** to make the [8+2] cycloaddition preferable.

**The Cycloaddition under Various Conditions; Temperature and Pressure Effects.** Under high-pressure conditions, the reaction proceeded quite rapidly; under ordinary pressure, much longer time was required, e.g., ca. 100 h, for 43%-conversion of **1** at 100 °C. However, the most remarkable difference in feature of the reactions of **1** with **2** and **3** was the formation of [8+2] cycloadducts in considerably high yields from **3**.

The ratio of [4+2] cycloadducts to [8+2] cycloadducts showed a decrease with increasing pressure, but relative product distributions within each of the [4+2] and [8+2] cycloadducts remained constant in the range of 1 to 10000 bar.

**Conclusion.** It is worthy of note that the dienophiles having same π-system, **2** and **3**, showed different product selectivities, and moreover, a formation of the [8+2] cycloadducts from **3** constitutes the unprecedented example. In this regard, a detailed theoretical study seems to be desirable, and will be a subject of forthcoming paper.

## Experimental

Elemental analyses were performed by Mrs. M. Miyazawa of this Institute. 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 CDCl₃, unless otherwise specified, and the chemical shifts expressed were in δ units. The 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 (2 cm³) of **1** (106 mg) and **2** (208 mg) was heated at 140 °C under 5000 bar for 24 h. The mixture was then separated by means of silica-gel column and high-pressure liquid (Microporasil, EtOAc and hexane) chromatography to give the products:

**9α-Phenyldihydrohomobarrelenone (4):** Colorless crystals, mp 101-102 °C (lit.[2] mp 101.6-102.8 °C), 114.8 mg; 55%. ¹H NMR $\delta$=2.12 (1H, ddd, $J$=13.9, 5.5, 5.1 Hz), 2.47 (1H, ddd, $J$=13.9, 9.9, 1.1 Hz), 3.33 (1H, dd, $J$=8.1, 7.7 Hz), 3.54 (1H, dd, $J$=9.9, 5.5 Hz), 3.63 (1H, dddm, $J$=8.1, 5.1, 2.2 Hz), 5.84 (1H, ddd, $J$=11.0, 2.2, 0.7 Hz), 6.34 (1H, dd, $J$=8.1, 7.7 Hz), 6.48 (1H, t, $J$=7.7 Hz), and 7.1-7.3 (6H, m). MS $m/z$ (%), 210 (M⁺, 54), 119 (15), 105 (11), 104 (100), 103 (11), 91 (18), 78 (15), and 77 (14).

**9β-Phenyldihydrohomobarrelenone (5):** A colorless oil (lit.[2] mp 80.5-82 °C), 59.5 mg; 28%. ¹H NMR $\delta$=2.13 (1H, dd, $J$=14.7, 8.1 Hz), 2.34 (1H, ddd, $J$=14.7, 9.5, 7.0 Hz), 3.27 (1H, td, $J$=8.4, 3.3 Hz), 3.47 (1H, ddd, $J$=9.5, 8.1, 3.3 Hz), 3.60 (1H, dddm, $J$=8.1, 7.0, 2.2 Hz), 5.96 (1H, ddm, $J$=11.0, 2.2 Hz), 6.09 (1H, ddd, $J$=8.1, 7.3, 0.7 Hz), 6.71 (1H, ddd, $J$=8.4, 7.3, 1.1 Hz), and 6.76 (1H, dd, $J$=11.0, 8.4 Hz), and 7.7-7.3 (5H, m). MS $m/z$ (%): 211 (M⁺+1, 13), 210 (M⁺, 76), 209 (11), 167 (11), 119 (17), 115 (35), 105 (10), 104 (100), 91 (24), 78 (17), 77 (14), and 51 (10).

**8α-Phenyldihydrohomobarrelenone (6):** A colorless oil, 16.4 mg; 8%. Found: $m/z$, 210.1045 (M⁺). Calcd for $C_{15}H_{14}O$: 210.1044. ¹H NMR $\delta$=1.83 (1H, ddd, $J$=13.2, 7.7, 4.0 Hz), 2.52 (1H, ddd, $J$=13.2, 9.5, 2.6 Hz), 3.3-3.5 (2H, m), 3.52 (1H, dm, $J$=7.3 Hz), 5.82 (1H, ddd, $J$=11.0, 2.2, 0.7 Hz), 6.19 (1H, ddd, $J$=8.4, 7.3, 1.1 Hz), 6.78 (1H, ddm, $J$=8.4, 7.3 Hz), 7.09 (1H, dd, $J$=11.0, 8.8 Hz), and 7.15-7.32 (5H, m). MS $m/z$ (%): 211 (M⁺+1, 16), 210 (M⁺, 100), 167 (35), 165 (17), 155 (53), 154 (29), 128 (15), 115 (27), 104 (68), 103 (19), 91 (32), 78 (24), 77 (32), and 51 (19). IR $\nu$: 2960, 2232, 1667, 1634, 1387, 1263, 829, and 713 cm⁻¹. UV $\lambda^{MeOH}_{max}$=226 nm ($\varepsilon$=5300, sh), 232 (5000, sh), 284 (1000), and 342 (500).

**8β-Phenyldihydrohomobarrelenone (7):** A colorless oil, 14.3 mg; 7%. Found: C, 85.93; H, 6.96%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. ¹H NMR $\delta$=2.30 (1H, ddd, $J$=13.6, 6.2, 1.5 Hz), 2.43 (1H, ddd, $J$=13.6, 10.6, 5.1 Hz), 3.43 (1H, ddd, $J$=10.6, 6.2, 5.1 Hz), 3.46 (1H, dddd, $J$=8.0, 7.7, 5.1, 1.5 Hz), 3.66 (1H, dddm, $J$=8.0, 5.1, 1.8 Hz), 5.89 (1H, ddd, $J$=11.0, 1.8, 0.7 Hz), 6.29 (1H, ddd, $J$=8.0, 7.7, 1.1 Hz), 6.57 (1H, t, $J$=7.7 Hz), 7.14-7.21 (3H, m), 7.23-7.30 (2H, m), and 7.33 (1H, dd, $J$=11.0, 8.0 Hz). MS $m/z$ (%): 211 (M⁺+1, 16), 210 (M⁺, 100), 167 (18), 155 (25), 154 (11), 115 (13), 104 (84), 103 (12), 91 (17), 78 (14), and 77 (16). IR $\nu$: 3028, 2940, 1662, 1632, 1494, 1385, 1157, 840, 760, 722, 701, and 680 cm⁻¹. UV $\lambda^{MeOH}_{max}$= 210 nm ($\varepsilon$=11400, sh), 232 (5300), 283 (1100), and 321 (400).

**Thermal Cycloaddition Reaction of 2 with 1 under Ordinary Pressure.** A toluene solution (4 cm³) of **1** (590 mg) and **2** (6 cm³) 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 **4, 5, 6,** and

**7** (117 mg; 16.5%) together with the recovered **2** (242 mg; 57%). Further fractionation was carried out by means of high-pressure liquid chromatography, and the results were compiled in Table 3.

**High-Pressure Cycloaddition Reactions of 1 and 3.** An acetonitrile solution (4 cm³) of **1** (106 mg), **3** (240 mg), and hydroquinone (20 mg) was heated at 100 °C under 8000 bar for 3 h. The mixture was then separated by means of silica-gel column and high-pressure liquid (Microporasil, EtOAc and hexane) chromatography to give the products:

**9β-Methyl-9α-phenyldihydrohomobarrelenone (9):** A colorless oil, 15.4 mg; 12%. Found: C, 85.68; H, 7.19%. Calcd for $C_{16}H_{16}O$: C, 85.76; H, 7.19%. $^1$H NMR $\delta=1.53$ (3H, s), 2.06 (1H, d, $J=15.0$ Hz), 2.83 (1H, ddd, $J=15.0$, 7.3, 1.1 Hz), 3.53 (1H, dddd, $J=8.4$, 7.3, 2.2, 1.1 Hz), 3.59 (1H, dd, $J=8.8$, 8.4 Hz), 5.90 (1H, ddm, $J=11.0$, 2.2 Hz), 5.98 (1H, ddd, $J=8.4$, 7.3, 1.1 Hz), 6.31 (1H, ddd, $J=8.4$, 7.3, 1.1 Hz), 7.09 (1H, dd, $J=11.0$, 8.8 Hz), 7.16 (1H, m), and 7.24—7.31 (4H, m). IR $\nu$: 3052, 2966, 1670, 1636, 1497, 1460, 1444, 1383, 815, 761, 749, 701, 681 cm⁻¹. UV $\lambda_{max}^{MeOH}=225$ nm ($\varepsilon=6800$) and 259 (2300, sh).

**9α-Methyl-9β-phenyldihydrohomobarrelenone (10):** A colorless oil, 15.5 mg; 12%. Found: C, 85.54; H, 7.10%. Calcd for $C_{16}H_{16}O$: C, 85.76; H, 7.19%. $^1$H NMR $\delta=1.38$ (3H, s), 2.21 (1H, dd, $J=14.3$, 7.0 Hz), 2.63 (1H, d, $J=14.3$ Hz), 3.58 (1H, ddd, $J=8.4$, 7.0, 2.2 Hz), 3.72 (1H, t, $J=8.4$ Hz), 5.60 (1H, dd, $J=11.0$, 2.2 Hz), 6.18 (1H, dd, $J=8.4$, 7.3 Hz), 6.65 (1H, ddd, $J=8.4$, 7.3, 1.1 Hz), 6.86 (1H, dd, $J=11.0$, 8.4 Hz), 7.18 (1H, m), and 7.27—7.40 (4H, m). MS $m/z$ (%): 224 (M⁺, 62), 209 (27), 120 (30), 119 (26), 118 (100), 117 (29), 115 (37), 107 (27), 105 (23), 103 (28), 91 (43), 78 (30), 77 (39), and 51 (24) and 39 (22). $\lambda_{max}^{MeOH}=229$ nm ($\varepsilon=6600$) and 258 (1700, sh).

**8β-Methyl-8α-phenyldihydrohomobarrelenone (11):** A colorless oil, 4 mg; 3%. Found: $m/z$, 224.1206 (M⁺). Calcd for $C_{16}H_{16}O$: 224.1201. $^1$H NMR $\delta=1.54$ (3H, s), 2.26 (1H, dd, $J=13.6$, 1.5 Hz), 2.52 (1H, dd, $J=13.6$, 5.1 Hz), 3.38 (1H, dddd, $J=8.4$, 7.3, 5.1, 1.5 Hz), 3.77 (1H, dd, $J=7.3$, 2.2 Hz), 5.83 (1H, ddd, $J=11.0$, 2.2, 0.7 Hz), 6.14 (1H, ddd, $J=8.4$, 7.3, 1.1 Hz), 6.56 (1H, dd, $J=8.4$, 7.3 Hz), 7.16 (1H, m), 7.19 (1H, dd, $J=11.0$, 8.4 Hz), and 7.23—7.38 (4H, m). MS $m/z$ (%): 224 (M⁺, 16), 209 (16), 118 (100), 117 (19), 115 (17), 107 (44), 91 (26), 78 (17), 77 (21), 55 (24) and 44 (17). IR $\nu$: 3052, 2966, 1664, 1633, 1582, 1497, 1443, 1384, 1260, 1243, 835, 761, 742, 701, and 681 cm⁻¹. UV $\lambda_{max}^{MeOH}=227$ nm ($\varepsilon=5300$, sh), 257 (1100 sh), and 305 (200).

***endo*-[8+2] Cycloadduct (12):** A colorless oil, 32 mg; 25%. Found: $m/z$, 224.1202 (M⁺). Calcd for $C_{16}H_{16}O$: 224.1201. $^1$H NMR $\delta=1.67$ (3H, s), 2.37 (1H, dd, $J=12.1$, 5.9 Hz), 2.73 (1H, dd, $J=12.1$, 9.2 Hz), 2.87 (1H, dddd, $J=9.2$, 5.9, 3.7, 1.8 Hz), 4.46 (1H, dd, $J=9.5$, 3.7 Hz), 5.79 (1H, d, $J=7.0$ Hz), 5.98 (1H, ddd, $J=9.5$, 5.9, 1.8 Hz), 6.20 (1H, dd, $J=11.0$, 5.9 Hz), 6.42 (1H, dd, $J=11.0$, 7.0 Hz), and 7.29—7.40 (5H, m). MS $m/z$ (%): 225 (M⁺+1, 10), 224 (M⁺, 60), 209 (20), 119 (11), 118 (100), 117 (21), 115 (11), 107 (29), 103 (14), 91 (11), 78

(11), and 77 (12). IR $\nu$: 3014, 2972, 1641, 1538, 1447, 1379, 1258, 1192, 1149, 1066, 917, 764, and 699 cm$^{-1}$. UV $\lambda_{max}^{MeOH} = 204$ nm ($\varepsilon = 4400$), 257 (2400), and 300 (3200).

   *exo*-[8+2] **Cycloadduct (13):** A colorless oil, 7.7 mg; 6%. Found: $m/z$, 224.1202 (M$^+$). Calcd for C$_{16}$H$_{16}$O: 224.1201. $^1$H NMR $\delta = 1.69$ (3H, s), 2.27 (1H, dd, $J = 12.1$, 7.7 Hz), 2.76 (1H, dddd, $J = 8.8$, 7.7, 3.3, 1.8 Hz), 2.90 (1H, dd, $J = 12.1$, 8.8 Hz), 4.97 (1H, dd, $J = 9.2$, 3.3 Hz), 5.79 (1H, d, $J = 7.0$ Hz), 6.07 (1H, ddd, $J = 9.2$, 5.9, 1.8 Hz), 6.14 (1H, dd, $J = 11.0$, 5.9 Hz), 6.34 (1H, dd, $J = 11.0$, 7.0 Hz), 7.25 (1H, m), and 7.29-7.42 (4H, m). MS $m/z$ (%): 225 (M$^+$+1, 12), 224 (M$^+$, 71), 209 (26), 119 (11), 118 (100), 117 (22), 115 (13), 107 (31), 103 (18), 91 (16), 78 (14), and 77 (18). IR $\nu$: 3014, 2976, 1642, 1543, 1495, 1446, 1377, 1258, 1202, 1147, 1069, 764, and 699 cm$^{-1}$. UV $\lambda_{max}^{MeOH} = 270$ nm ($\varepsilon = 11400$, sh), 262 (1100), and 302 (3000).

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### 和 文 概 要

   スチレン，α-メチルスチレンとトロポンの高圧環状付加反応を行った所，前者からは4種の可能な〔4＋2〕付加体（ジヒドロホモバーレレノン）総てが生成した。一方，後者からは3種の〔4＋2〕付加体と共に2種類の〔8＋2〕付加体が生成した。特に，この〔8＋2〕付加体の生成はヘテロ原子を置換していないオレフィンとの反応では初めての知見である。