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Cycloaddition-Cycloreversion Sequence for One-pot Preparation of Dibenzobarrelene and Janusene Derivatives from Anthracenes and 2, 3-Bis-(methoxycarbonyl)-7-oxanorbornadiene

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Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

Dibenzobarrelenes can be prepared by Diels-Alder reaction of anthracenes with 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene followed by thermal cycloreversion in good yields; sterically-hindered 9,10-dimethylanthracene smoothly furnished a corresponding dimethyl derivative even in a better yield. In the same time, janusene derivatives were obtained as by-products by successive cycloaddition-cycloreversion processes under one-pot formation conditions.

Chemical reactions of dibenzobarrelenes (**1**)[1] are attracting considerable attentions in view of transannular charge transfer phenomenon between three spacially-oriented π -electron systems.[2] And thus, development of their effective method of synthesis is still a current interest, but only limited derivatives could be efficiently prepared by the known methods. Meanwhile, Butler et al. intensively explored a route to **1** from the Diels-Alder adducts of anthracenes (**2**) to dienophiles, such as norbornadiene, but the result was not really satisfactory.[3] Recently, we have prepared homobarrelenones [4] via a cycloaddition-cycloreversion procedure of tropones to 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene (**3**). This paper deals with a facile one-step synthesis of **1** via a similar sequence.

When several **2** and **3** were heated in dimethyl sulfoxide, the formation of cycloadducts was recognized. Silica-gel column and/or high-pressure liquid chromatography led to isolate the products (**4** and **5**). By-products (**5**), obtained in all cases, were formed by the addition of **2** and dimethyl butynedioate which might be formed via cycloreversion of **3**.

Further heating of **4** at 210 °C yielded **1** together with 3,4-bis(methoxycarbonyl)furan (**6**). Table 3 summarizes the ^{1}H NMR data of the thermolysates, **1**. Consequently, **1** can be

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prepared from **2** and **3** in a one-pot manner without isolation of the intermediates **4**.

Furthermore, when a mixture of **2** and **3** was heated at 190 °C to cause a one-pot formation of **1**, the other type of by-products, 2:1-adducts (**7**), janusene derivatives, were produced. Presumably, the yields of **7** could be improved by heating 2:1-mixtures of **2** and **3** at that temperature.

In the ^{1}H NMR, characteristic signals of the methyl group at the bridge-head positions of **1b** or **1c** appeared at ca. δ=2.15, that is more down-field shifted than those methyls on the typical sp^2-carbons; three-fold anisotropy from the π-electrons attributed to this. The ^{13}C

Table 1. Diels Alder Reaction of **2** and **3**.

		Yields / % of Products (mp / ℃)	
2	Conditions	**4**	**5**
2a	140 ℃, 2 d	64 (204—205)	19 (156—157.5)[a]
2b	140 ℃, 2 d	64 (164—165)	26 (183—184)[b]
2c	140 ℃, 2 d	78 (159—160)	14 (180)[c]

a) Ref. 5. b) Ref. 6. c) Ref. 7.

Table 2. The ^{1}H NMR Spectra of the Diels-Alder Adducts (**4**)

4	**4a**	**4b**	**4c**
		NMR Chemical Shifts[a]	
H—1	4.37	——	——
H—2	2.46	2.13 (d, 8.1)	2.21
H—3	4.80	4.82*[b]	4.86
H—6	4.80	4.83*	4.86
H—7	2.46	2.53 (dd, 8.1, 2.9)	2.21
H—8	4.37	4.36 (d, 2.9)	——
Me	3.75	2.03, 3.75, 3.76	2.04, 3.76
Ar	7.0 — 7.3 (m)	7.0 — 7.3 (m)	7.0 — 7.3 (m)

a) Chemical shifts were expressed in δ unit in $CDCl_3$, and the multiplicities and coupling constants were shown in parentheses.

b) Asterisked assignments may be reversed.

Table 3. The ^{1}H NMR Spectra of **1**

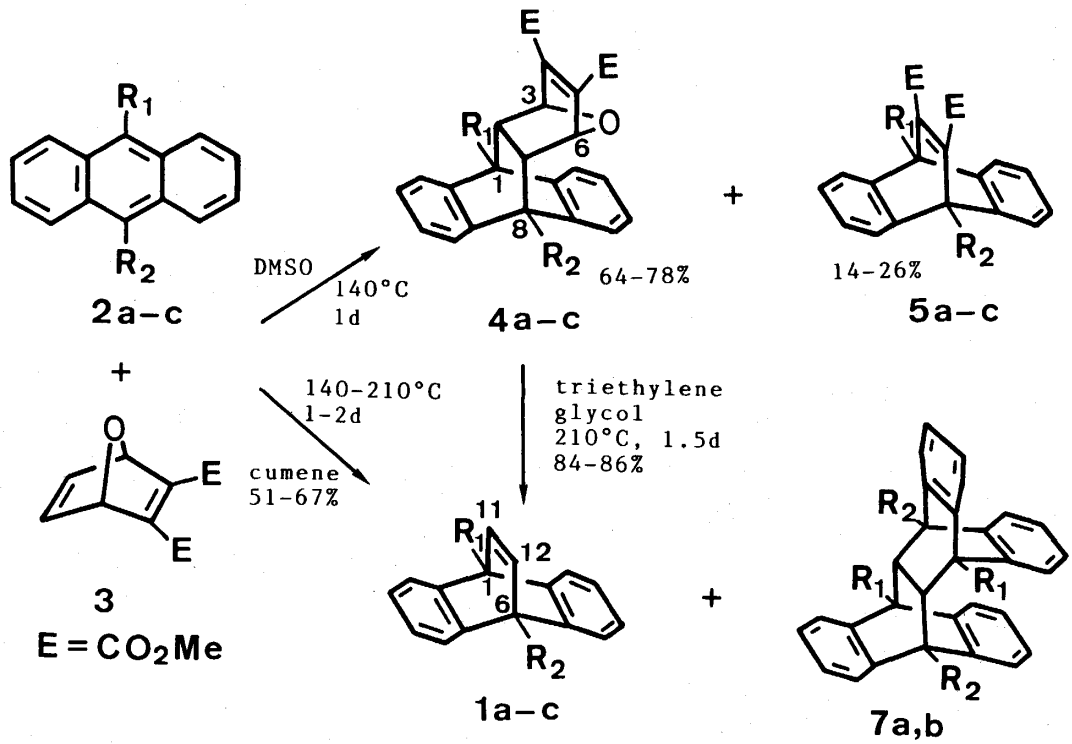
1a : 5.1 — 5.15 (2 H, m), 6.9 — 7.0 (6 H, m), and 7.2 — 7.3 (4 H, m).

1b : 2.16 (3 H, s), 5.08 (1 H, dd, J = 5.9, 1.5 Hz), 6.60 (1 H, dd, J = 7.0, 1.5 Hz), 6.9 — 7.0 (4 H, m), 7.03 (1 H, dd, J = 7.0, 5.9 Hz), and 7.2 — 7.3 (4 H, m).

1c : 2.15 (6 H, s), 6.64 (2 H, s), 6.9— 7.1 (4 H, m), and 7.2 — 7.3 (4 H, m).

NMR chemical shifts of the dibenzobarrelenes also revealed a good correlation to the substituent.

Since this simple procedure gives **1** in high yields, this must have a general applicability; particularly, a smooth reaction with 9,10-dimethylanthracene assures that even sterically hindered derivatives can be prepared with no difficulty.



a: $R_1=R_2=H$, b: $R_1=Me, R_2=H$, c: $R_1=R_2=Me$

Experimental

Elemental analyses were performed by Miss S. Hirashima, of this Institute. The NMR spectra were measured in $CDCl_3$ with a JEOL FX 100 Spectrometer, and the chemical shifts were expressed in δ values. The mass spectra were measured with a JEOL OISG-2 Spectrometer. The IR spectra were taken as liquid films or KBr disks using a Jasco IR-A 102Spectrometer. The UV spectra were measured by a Hitachi U-3200 Spectrophotometer.

Diels-Alder Reaction of 2a and 3. A dimethyl sulfoxide solution (2 cm^3) of anthracene (**2a**, 378 mg) and **3** (450 mg) is heated at 140 °C for 2 d. The mixture was then directly chromatographed on a silica-gel column (Wako-Gel C-300, 30 g) with AcOEt-hexane to give **4a** [colorless crystals, mp 204–205 °C, 349.5 mg; 64%. Found: C, 74.10; H, 5.14%. Calcd for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19%. ^{13}C NMR δ=46.9 (2C), 47.2 (2C), 52.2 (2C), 83.1 (2C), 123.8 (4C), 125.9 (2C), 126.2 (2C), 141.1 (2C), 144.1 (2C), 145.5 (2C), and 162.9 (2C). IR ν: 1735, 1715, 1635,

and 1220 cm^{-1}] and **5a** [colorless crystals, mp 156–157 °C (*lit.*[5] 160–161 °C), 84.6 mg; 19%. ^1H NMR δ=3.77 (6H, s), 5.47 (2H, s), 6.95–7.05 (4H, m), and 7.35–7.45 (4H, m). ^{13}C NMR δ=52.4 (2C), 52.5 (2C), 123.8 (4C), 125.4 (4C), 143.8 (4C), 147.0 (4C), and 165.9 (2C). IR ν: 1720, 1640, and 1270 cm^{-1}], along with the recovered **2a** (127 mg).

Diels-Alder Reaction of 2b and 3. A dimethyl sulfoxide solution (2 cm^3) of 9-methylanthracene (**2b**, 387 mg) and **3** (450 mg) is heated at 140 °C for 2 d. After evaporation of the solvent, the residue is chromatographed on a silica-gel column (Wako-Gel C-300, 30 g) with AcOEt-hexane to give **4b** [colorless crystals, mp 164–165 °C, 342.9 mg; 64%. Found: C, 74.46; H, 5.48%. Calcd for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51%. ^{13}C NMR δ=15.9, 43.8, 47.1, 48.6, 52.2 (2C), 52.6, 81.4, 83.4, 121.2, 121.4, 123.5, 123.6, 125.8 (2C), 126.0 (2C), 141.5, 143.2, 144.6, 145.4, 145.5, 146.4, 162.8, and 162.9. IR ν: 1730, 1710, 1620, and 1220 cm^{-1}] and **5b** [colorless crystals, mp 183–184 °C (*lit.*[6] 180 °C), 114 mg; 26%. ^1H NMR δ=2.15 (3H, s), 3.73 (3H, s), 3.80 (3H, s), 5.64 (1H, s), 7.0–7.1 (4H, m), and 7.3–7.4 (4H, m). ^{13}C NMR δ=12.3, 50.1, 51.5, 52.2, 52.4, 121.1 (2C), 123.6 (2C), 125.1 (2C), 125.3 (2C), 142.0, 145.5 (2C), 145.7 (2C), 155.5, 163.8, and 167.5], along with the recovered **2b** (131.4 mg).

Diels-Alder Reaction of 2c and 3. A dimethyl sulfoxide solution (1.5 cm^3) of 9,10-dimethylanthracene (**2c**, 318 mg) and **3** (330 mg) is heated at 140 °C for 2 d. After evaporation of the solvent, the residue is chromatographed on a silica-gel column (Wako-Gel C-300, 30 g) with AcOEt-hexane to give **4c** [colorless crystals, mp 159–160 °C, 337 mg; 78%. Found: C, 75.00; H, 5.84%. Calcd for $C_{26}H_{22}O_5$: C, 74.98; H, 5.81%. ^{13}C NMR δ=16.5 (2C), 43.5 (2C), 52.4 (2C), 54.3 (2C), 81.9 (2C), 121.0 (2C), 121.4 (2C), 125.8 (2C), 126.0 (2C), 143.8 (2C), 145.7 (2C), 147.2 (2C), and 163.0 (2C). IR ν: 1730 and 1635 cm^{-1}] and **5c** [colorless crystals, mp 180 °C (*lit.*[7] 175–180 °C), 55 mg; 14%. ^1H NMR δ=2.26 (6H, s), 3.69 (6H, s), 7.0–7.1 (4H, m), and 7.3–7.4 (4H, m). ^{13}C NMR δ=13.6 (2C), 49.7 (2C), 51.9 (2C), 120.8 (4C), 124.9 (4C), 147.4 (4C), 150.2 (2C), and 166.0 (2C). IR ν: 1725, 1715, and 1620 cm^{-1}], along with the recovered **2c** (105 mg).

Cycloreversion of 4a to 1a. A triethylene glycol solution (1 cm^3) of **4a** (119 mg) was heated at 210 °C for 36 h. After removal of the solvent, the residue is chromatographed on a silica-gel column to give **1a** [colorless needles, mp 120 °C (*lit.*[8] mp 118–119 °C), 52 mg; 83%. ^{13}C NMR δ=51.3 (2C), 123.0 (4C), 124.4 (4C), 139.4 (2C), and 146.2 (4C). λ_{max}^{MeOH}: 211 nm (ε=37400), 215 (40300), 272 (2600), and 279 (3950)].

Cycloreversion of 4b to 1b. A triethylene glycol solution (2 cm^3) of **4b** (60 mg) is heated at 210 °C for 36 h. After removal of the solvent, the residue is chromatographed on a silica-gel column to give **1b** [colorless needles, mp 94–96 °C (*lit.*[9] mp 98–100 °C), 28 mg; 86%. ^{13}C NMR δ=15.1, 49.8, 51.3, 120.1 (2C), 122.7 (2C), 124.1 (2C), 124.2 (2C), 140.4, 143.9, 147.3 (2C), and 148.4 (2C). λ_{max}^{MeOH}: 211 nm (ε=35000), 216 (37500), 272 (2800), and 279 (3700).

Cycloreversion of 4c to 1c. A triethylene glycol solution (2 cm^3) of **4c** (69 mg) is heated at 210 °C for 36 h. After removal of the solvent, the residue is chromatographed on a silica-gel

column to give **1c** [colorless needles, mp 114–115 °C (*lit.*[9] mp 117–119 °C), 32.3 mg; 84%. ^{13}C NMR δ=15.4 (2C), 49.4 (2C), 119.7 (4C), 123.9 (4C), 144.9 (2C), and 149.5 (4C). λ_{max}^{MeOH}: 212 nm (ε=36400), 216 (39200), 271 (2300), and 279 (3500).

One-pot Preparation of 1a. A cumene solution (1.5 cm^3) of **2a** (90 mg) and **3** (130 mg) is heated at 140 °C for 2 d and then at 210 °C for 1 d. After removal of the volatile material in vacuo, the residue was chromatographed on a silica-gel column to give **1a** (10.3 mg; 35%) and **7a** [colorless crystals, mp 230–232 °C (*lit.*[10] 235–238 °C). 9.7 mg; 17.4%. ^{13}C NMR δ=45.1 (2C), 49.1 (4C), 122.9 (4C), 125.4 (4C), 125.6 (4C), 125.7 (4C), 140.4 (4C), and 145.8 (4C)], together with **6** (13 mg), **5a** (21 mg; 45%), and the recovered **2a** (64 mg).

One-pot Preparation of 1b. A cumene solution (1.5 cm^3) of **2b** (97 mg) and **3** (133 mg) is heated at 140 °C for 2 d and then at 210 °C for 1 d. The mixture was then separated on a silicagel column and a preparative thin-layer chromatography to give **1b** (25.6 mg; 41%) and **7b** [colorless crystals, mp 285 °C, 8.8 mg; 8%. Found: C, 93.59; H, 6.31%. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38%. ^{1}H NMR δ=2.05 (6H, s), 2.29 (2H, s), 4.29 (2H, s), and 6.67–7.2 (16H, m). ^{13}C NMR δ=15.6 (2C), 44.9 (2C), 46.2 (2C), 51.0 (2C), 119.8 (2C), 122.9 (2C), 123.3 (2C), 124.9 (2C), 125.1 (2C), 125.2 (2C), 125.3 (2C), 125.6 (2C), 140.2 (2C), 142.4 (2C), 145.5 (2C), and 148.6 (2C)], together with **6** (28 mg; 52%), **5b** (45 mg; 46%), and the recovered **2b** (41.7 mg).

One-pot Preparation of 1c. A cumene solution (1 cm^3) of **2c** (104 mg) and **3** (130 mg) is heated at 140 °C for 2 d and then at 210 °C for 1 d. After removal of the volatile material in vacuo, the residue was chromatographed on a silica-gel column to give **1c** (43.4 mg; 67%), together with **6** (22.4 mg; 43%), **5c** (23.7 mg; 24%), and the recovered **2c** (46.3 mg).

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