A Facile Synthesis of Dibenzobarrelenes from 2,3-Bis(methoxy-carbonyl)-7-oxabicyclo[2.2.1]heptadiene with Anthracenes. Substituent Effect on the ^1H- and ^<13>C-NMR Spectra

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A Facile Synthesis of Dibenzobarrelenes from 2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene with Anthracenes. Substituent Effect on the ^{1}H- and ^{13}C-NMR Spectra

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Abstract. Dibenzobarrelenes were prepared by the cycloaddition-cycloreversion procedure from 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene and several anthracene derivatives. Substituent effects on the ^{1}H- and ^{13}C-NMR chemical shifts were discussed.

Recently, we have shown that 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1**) is a useful acetylene substitute. Using this method, homobarrelenones were conveniently prepared from **1** and tropones.[1] This prompted us to extend the procedure to prepare the dibenzobarrelene derivatives from anthracene derivatives (**2**). Previously there is an attempt of such a dibenzobarrelene synthesis by means of cycloaddition with anthracenes and norbornadiene (**A**) and subsequent fragmentation, but this was not very much successful.[2]

Herein, we will show an improved synthesis of dibenzobarrelenes from **1** and **2.** In the same time, a substituent effect of the ^{1}H- and ^{13}C-NMR chemical shifts is discussed.

When the thermal addition reaction of **1** with 9-bromoanthracene (**2a**) was carried out at 140 ℃ for 2 d, two products (**3a** and **4a**) were formed and isolated via silica-gel column chromatography in 76% and 23% yields, respectively. The **3a** was a 1:1-adduct of **1** and **2a,** and it was identified to be an *exo*-[4+2]cycloadduct from its NMR spectrum, in which the coupling constant of the protons on the bridge-head carbons bearing the ethereal oxygen was $J = 1.1$ to 1.5 Hz. The latter **4a** was identified as a formal 1:1-adduct of **2a** and dimethyl butynedioate (**5**) by comparing the ^{1}H- and ^{13}C-NMR spectra.[3] It is likely that **4a** was derived from a cycloadduct of **1** and **2a** at the different site, and spontaneous cycloreversion should be interpreted in terms of the severe steric hindrance of the intermediate adduct. Discussions on this regard will be a subject of an independent paper.

Similarly, the reactions of **1** and 9-cyanoanthracene (**2b**) and 9,10-dibromoanthracene (**2c**) gave similar *exo*-[4+2]cycloadducts (**3b** and **3c**) and the 1:1-cycloadduct (**4b**[4]) of **2b** to **5.** Their NMR spectra were compatible to their formulations.

The cycloreversion of **3** at 210 ℃ gave dibenzobarrelenes (**6a** to **6c**) in good yields together with small amounts of **2** (ca. 3% yields, respectively). The results were considerably improved from the previous report by Butler et al.,[2] i.e., the thermolysis of the **2d-A** adduct at 400 ℃ gave a mixture of **2d, 6d,** and cyclopentadiene in a ratio of 1:1:1. The

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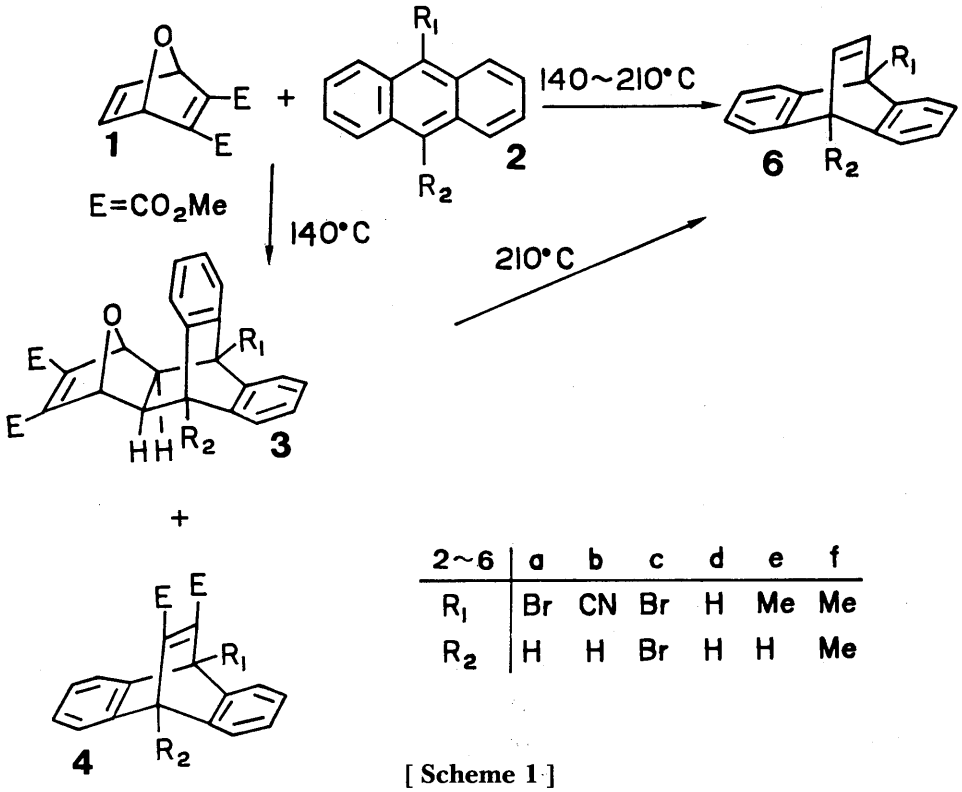

2~6	a	b	c	d	e	f
R_1	Br	CN	Br	H	Me	Me
R_2	H	H	Br	H	H	Me

[**Scheme 1**]

predominant formation of **6** from **3** must be due to a facile tendency of the cycloreversion of the Diels-Alder adducts of the furans in general.

While the solution of **1** and **2** was heated at 140 ℃ for 2 d and then at 210 ℃ for 1 d, **6** were formed in the one-pot manner with practical yields.

The entire ^{1}H- and ^{13}C-NMR data were tabulated in **Table 1** together with unsubstituted (**6d**), 1-methyl- (**6e**), and 1,6-dimethyl- (**6f**) derivatives.[5] In the ^{13}C-NMR spectra of **6a** and **6c,** the effect of the bromine introduction was ca. + 5 ppm, but the ^{1}H chemical shifts changed slightly.

In the ^{1}H-NMR spectrum of **6e,** the chemical shift of H-b was ca. 0.4 ppm higher than that of H-c. This was parallel to benzobarrelene (δ = 6.84)[6] and 1-methylbenzobarrelene (δ = 6.42).[7] These high-field shifts due to a methyl group would be explained by the shielding effect of C-Me bond.

Next, the substituent effect of the bromine and methyl group on the ^{13}C chemical shifts showed an additivity. The methyl group in **6e** showed a shift of + 4.5 ppm for b-carbon and + 1.0 ppm for c-carbon. The olefinic carbons (C-b and C-c) in **6f** appeared at 144.9 ppm, which was shifted by + 5.5 ppm. While the introduction of bromine to **6a** caused a shift by + 5.4 ppm for b-carbons and by − 0.2 ppm for c-carbons, the etheno carbons in **6c** appeared at 144.5 ppm, and by + 5.1 ppm. Similar additivity was also observed in bis-(methoxycarbonyl) derivatives (**4**) as shown in **Table 1.**

Table 1 NMR Data of Dibenzobarrelenes (**4** and **6**)[a]

R_1	R_2		C-a	C-b	C-c	C-d
H	H	**6d**	51.3	139.4	139.4	51.3
		4d	[52.4]	[147.0]	[147.0]	[52.4]
Me	H	**6e**	49.8(−1.5)	143.9(+4.5)	140.4(+1.0)	51.3(0)
		4e	[51.5] (−0.9)	[155.5] (+8.5)	[142.0] (−5.0)	[52.4] (0)
Br	H	**6a**	67.0(+15.7)	144.8(+5.4)	139.2(−0.2)	50.7(−0.6)
		4a	[66.6] (+14.2)	[154.2] (+7.2)	[140.5] (−6.5)	[49.8] (−2.6)
CN	H	**6b**	51.0(−0.3)	137.3(−2.1)	140.7(+1.3)	50.3(−1.0)
		4b	[53.6] (+1.2)	[143.1] (−3.9)	[147.9] (+0.9)	[53.0] (+0.6)
Me	Me	**6f**	49.4(−1.9)	144.9(+5.5)	144.9(+5.5)	49.4(−1.9)
		4f	[49.7] (−2.7)	[150.2] (+3.2)	[150.2] (+3.2)	[49.7] (−2.7)
Br	Br	**6c**	65.5(+14.2)	144.5(+5.1)	144.5(+5.1)	65.5(+14.2)
			H-a	H-b	H-c	H-d
H	H	**6d**	5.13	7.0	7.0	5.13
Me	H	**6e**	—	6.60(−0.4)	7.03(+0.03)	5.08(−0.05)
Br	H	**6a**	—	7.05(+0.05)	6.95(−0.05)	5.09(−0.04)
CN	H	**6b**	—	6.97(−0.03)	7.13(+0.13)	5.18(+0.05)
Me	Me	**6f**	—	6.64(−0.36)	6.64(−0.36)	—
Br	Br	**6c**	—	7.02(+0.02)	7.02(+0.02)	—

[a] Numbers in brackets are data of **4**. Numbers in parentheses are differences between unsubstituted and substituted dibenzobarrelenes. +: low field shift. −: high field shift.

Consequently, the cycloaddition-thermal cycloreversion reactions of **1** and **2** are useful for preparing dibenzobarrelenes derivatives. Different temperatures for addition and cycloreversion made operations easy and the yields of **3** were quite high, and this investigation further confirms a versatility of **1** as an acetylene equivalent.

Experimental

The elemental analyses were carried out by Miss S. Hirashima, of this Institute. The NMR spectra were measured by a JEOL GSX 270 Spectrometer in $CDCl_3$ solution, and the chemical shifts expressed were in δ unit. The IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 Spectrometer.

Diels-Alder Reaction of 1 and Anthracenes (2a-d) (General Procedure). A dimethyl sulfoxide (DMSO) solution of **1** and **2** was heated at 140 ℃ for 2 d. Removal of DMSO by distillation in vacuo left a brown residue which afforded **3** and **4** via silica-gel column chromatography.

3a: colorless crystals, mp 223 − 224 ℃, 76%. Found: C, 61.49; H, 4.08%. Calcd for $C_{24}H_{19}O_5Br$: C, 61.69; H, 4.10%. ^{1}H NMR δ =2.61 (1H, ddd, J=8.1, 2.9, 1.5 Hz), 2.80 (1H, dd, J=8.1, 1.1 Hz), 3.77 (3H, s), 3.78 (3H, s), 4.41 (1H, d, J=2.9 Hz), 4.87 (1H, d, J=1.5 Hz), 5.08 (1H, d, J=1.1 Hz), 7.1−7.3 (6H, m), and 7.6−7.75 (2H, m). ^{13}C NMR δ =46.6, 49.5, 52.3, 56.9, 69.9, 83.0, 83.5, 85.1, 123.2 (2C), 124.5, 124.8, 126.3, 126.6, 127.1, 127.4, 139.4, 139.9, 142.4, 143.1, 145.5, 145.7, 162.5, and 162.7. IR ν: 1730, 1710, 1630, 1290, and 1220 cm^{-1}.

4a: colorless crystals, mp 179−180 ℃ (lit.[3] 175−177 ℃), 23%, ^{1}H NMR δ =3.75 (3H, s), 3.84 (3H, s), 5.68 (1H, s), 7.05−7.15 (4H, m), 7.35−7.4 (2H, m), and 7.7−7.75 (2H, m).

3b: colorless crystals, mp 185−187 ℃, 93%. Found: C, 72.57; H, 4.61; N, 3.26%. Calcd

for $C_{25}H_{19}NO_5$: C, 72.63; H, 4.63; N, 3.39%. ^{1}H NMR δ =2.59 (1H, dd, J=8.1, 2.9 Hz), 2.73 (1H, d, J=8.1 Hz), 3.78 (3H, s), 3.80 (3H, s), 4.46 (1H, d, J=2.9 Hz), 4.83 (1H, d, J=1.1 Hz), 5.02 (1H, s), 7.15−7.35 (6H, m), and 7.55−7.65 (2H, m). ^{13}C NMR δ =46.1, 47.5, 51.9, 52.4, 60.4, 82.0, 83.0, 117.8, 122.3, 122.5, 124.3 (2C), 126.7, 127.0, 127.7, 127.9, 135.7, 138.9, 139.0, 142.0 (2C), 145.0, 145.9, 162.1, and 162.5. IR ν: 1710, 1635, and 1280 cm^{-1}.

4b: colorless crystals, mp 186 ℃ (lit.[4] 174−175 ℃), 7%. ^{1}H NMR δ =3.78 (3H, s), 3.89 (3H, s), 5.66 (1H, s), 7.1−7.2 (4H, m) 7.4−7.5 (2H, m), and 7.65−7.75 (2H, m).

3c: colorless crystals, mp 191 − 192 ℃, 82%. Found: C, 52.71; H, 3.35%. Calcd for $C_{24}H_{18}O_5Br_2$: C, 52.78; H, 3.32%. ^{1}H NMR δ =2.94 (2H, s), 3.79 (6H, s), 5.15 (2H, s), 7.2−7.3 (4H, m), and 7.6 − 7.8 (4H, m). ^{13}C NMR δ =52.4 (2C), 58.9 (2C), 68.5 (2C), 83.7 (2C), 124.1 (2C), 124.4 (2C), 127.6 (2C), 127.8 (2C), 138.3 (2C), 141.6 (2C), 145.7 (2C), and 162.3 (2C). IR ν: 1735 and 1640 cm^{-1}. UV λ_{max}^{MeOH}: 207 nm (ε =42000).

Thermolysis of 3. Formation of 6. A triethylene glycol solution of **3** was heated at 210 ℃ for 26 h. Removal of the solvent by distillation in vacuo left a syrup. Silica-gel column chromatography gave **6** along with **2** (3%).

5a: colorless crystals, mp 139 − 140 ℃, 87%. Found: C, 68.08; H, 3.89%. Calcd for $C_{16}H_{11}Br$: C, 67.87; H, 3.92%, ^{1}H NMR δ =5.09 (1H, dd, J=5.9, 1.8 Hz), 6.95 (1H, dd, J=7.3, 5.9 Hz), 7.05 (1H, dd, J=7.3, 1.8 Hz), 6.9−7.1 (4H, m), 7.2−7.3 (2H, m), and 7.65−7.7 (2H, m). IR ν: 1595, 1580, 1450, 1435, 950, 750, 735, and 670 cm^{-1}. UV λ_{max}^{MeOH}: 211 nm (ε =40800), 214 (45600), 271 (2100), and 278 (2900).

5b: colorless crystals, mp 113−115 ℃, 86%. Found: C, 89.05; H, 4.77; N, 5.91%. Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11%. ^{1}H NMR δ =5.18 (1H, dd, J=5.9, 1.5 Hz), 6.97 (1H, dd, J=7.0, 1.8 Hz), 7.13 (1H, dd, J=7.0, 5.9 Hz), 7.05−7.15 (4H, m), 7.3−7.35 (2H, m), and 7.6 −7.65 (2H, m). IR ν: 2230, 1450, 757, 745, and 677 cm^{-1}. UV λ_{max}^{MeOH}: 209 nm (ε = 38000), 214 (44500), 255 (7500), 278 (2000), 278 (2700), and 363 (685).

5c: colorless crystals, mp 104 − 105 ℃, 89%. Found: C, 53.00; H, 2.88%. Calcd for $C_{16}H_{10}Br_2$: C, 53.08; H, 2.78%. ^{1}H NMR δ =7.02 (2H, s), 7.05−7.15 (4H, m), and 7.65−7.7 (4H, m). IR ν: 1595, 1450, 1430, 955, 755, 740, and 655 cm^{-1}. UV λ_{max}^{MeOH}: 213 nm (ε= 44700), 270 (1500), and 277 (1800).

One-pot Preparation of 6. Each mixture of **1** and **2** was heated at 140 ℃ for 2 d and then at 210 ℃ for 1 d. Removal of the solvent by distillation in vacuo and subsequent silica-gel column chromatography gave **6,** i.e., **6a** [75%], **6b** [75%], **6c** [76%], **6e** [51%], and **6f** [67%], respectively, which were identical with the authentic samples.

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