

¹H AND ¹³C NMR SPECTRA OF BISHOMOBENZOBARRELENES¹

Keizo Kitahonoki, Kensuke Sakurawi, Kazuo Tori* and Masako Ueyama

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

(Received in Japan 29 November 1975, received in UK for publication 16 December 1975)

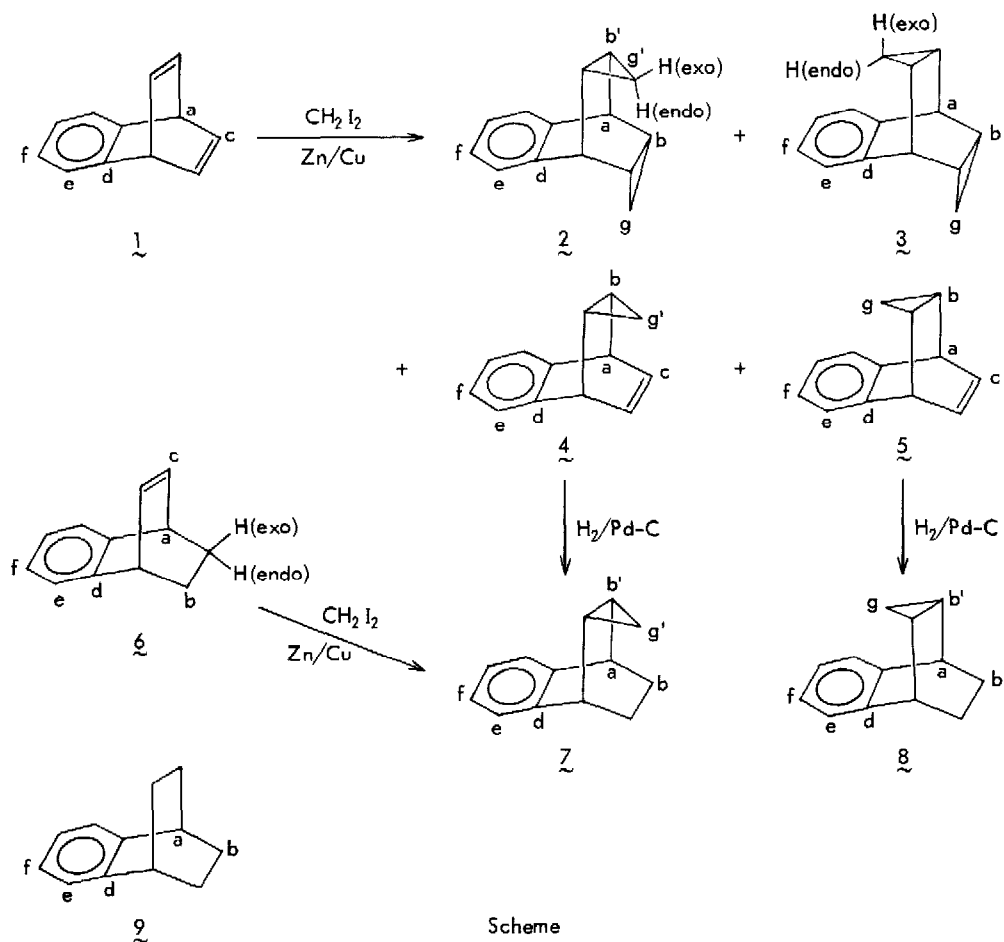
In the course of our ¹H NMR studies of the shielding effects exerted by a cyclopropane ring,² we synthesized two isomeric bishomobenzobarrelenes, *exo,endo*- and *endo,endo*-benzotetracyclo[3.3.2.0^{2,4}.0^{6,8}]-decenes (2 and 3, respectively), and related compounds 4, 5, 7, and 8 to test the applicability of the known rule for cyclopropane anisotropy^{2,†} Some anomalies in ¹H and ¹³C chemical shifts were found in the spectra of 3, although the spectra of the other compounds generally showed features expected as a whole

Structural assignments of the compounds were based on their 100-MHz ¹H NMR spectra. Detailed examinations of the spectra by double and triple resonance techniques gave the signal assignments. The TABLE lists the δ_{H} data obtained together with the signal shift ($\Delta\delta_{\text{H}}$) values due to introduction of a cyclopropane ring

Comparisons of the δ_{H} values between 7, 8, and 9⁴ revealed that the ethano-bridge protons, H_{b(exo)} and H_{b(endo)}, in 7 are more shielded by the cyclopropane-ring anisotropy,^{2,3} and that the cyclopropane geminal protons, H_{g(exo)} and H_{g(endo)}, in 8 are much shielded by the ring-current effect of the benzene

[†] Simmons-Smith reaction⁵ of benzobarrelene (1)^{6a, b} led to a mixture of 2 and 3 together with two isomeric homobenzobarrelenes (4 and 5) which were separated by TLC to give pure colorless prisms, 2 in 4.9% yield, m p 92-93° [ν_{max} (Nujol) 3005, 3050, and 1025 cm⁻¹], 3 in 4.8% yield, m p 131-132° [ν_{max} (Nujol) 3045, 3010, 1023, and 703 cm⁻¹], 4 in 23.2% yield, m p 47-48.5° [ν_{max} (Nujol) 3070, 3020, 1015, and 695 cm⁻¹], and 5 in trace, m p 43°. *Exo*- and *endo*-benzotricyclo[3.2.2.0^{2,4}]nonenes (7 and 8, respectively) were prepared from benzobicyclo[2.2.2]octadiene (6)^{6b, c} by the same reaction. 7 in 0.1% yield, m p 62-63° [ν_{max} (Nujol) 3005, 3080, and 1026 cm⁻¹] and 8 in 40.5% yield, m p. 76-77° [ν_{max} (Nujol) 3071, 3010, 1032, and 998 cm⁻¹]. Hydrogenation of 4 and 5 on Pd-C afforded 7 and 8, respectively. See the Scheme

ring ⁴ Similarly, the cyclopropane-ring anisotropy shields the ethylenic protons H_c in 4 and deshields those in 5 as compared with those in 6.⁴ These observations assessed the structures of 7 and 8 as well as those of 4 and 5 as shown in the Scheme. The structures of 2 and 3 were easily assigned, the spectrum of the latter shows the degenerate ¹H signals due to the two cyclopropane rings, one of which also appeared at a considerably higher field (δ -0.77), clearly showing that 3 is endo,endo-bishomobenzobarrelene.



Scheme

As can be seen from the TABLE, the H_{g(exo)} and H_{g(endo)} signals were shifted downfield by +0.22 and +0.19 ppm, respectively, on going from 8 to 3, contrary to the expectation that they would be shifted upfield by the anisotropy of the cyclopropane introduced, whereas the signal shifts from 7 to 2 and 8 to 2 showed values expected with the anisotropy.

TABLE ^1H (δ_{H}) and ^{13}C (δ_{C}) Chemical Shift Data^a

Compound		a	b	b'	c	Position			g	g'
						d	e ^{b,c}	f ^{b,c}		
<u>9</u> ⁴	δ_{H}	2.93	1.74(exo) ^b 1.40(endo)	-	-	-	7.02	-	-	-
<u>7</u>	δ_{H}	3.05	1.60(exo) ^b 1.07(endo)	1.07	-	-	7.02	-	0.74(exo) 1.09(endo)	-
<u>7-9</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.12	-0.14(exo) -0.33(endo)	-	-	-	0.00	-	-	-
<u>8</u>	δ_{H}	3.18	1.75(exo) ^b 1.35(endo)	1.05	-	-	6.91	7.03	-0.11(exo) -0.96(endo)	-
<u>8-9</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.25	0.01(exo) -0.05(endo)	-	-	-	-0.11	0.01	-	-
<u>2</u>	δ_{H}	3.31	0.86	0.98	-	-	6.93	7.00	-0.18(exo) -1.05(endo)	0.70(exo) 1.74(endo)
<u>2-7</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.26	-0.74(exo)	-0.09	-	-	-0.09	-0.02	-	-0.04(exo) 0.65(endo)
<u>2-8</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.13	-0.37(endo)	-0.19	-	-	0.02	-0.03	-0.07(exo) -0.09(endo)	-
<u>3</u>	δ_{H}	3.42	1.28	-	-	-	6.82	7.07	0.11(exo) -0.77(endo)	-
<u>3-8</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.24	-0.47(exo)	0.23	-	-	-0.09	0.04	0.22(exo) 0.19(endo)	-
<u>6</u> ⁴	δ_{H}	3.84	1.49(exo) ^b 1.44(endo)	-	6.40	-	7.00	6.94	-	-
<u>4</u>	δ_{H}	3.86	1.16	-	6.04	-	7.02	6.88	-	0.76(exo) 0.56(endo)
<u>4-6</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.02	-0.28(endo)	-	-0.36	-	0.02	-0.06	-	-
<u>5</u>	δ_{H}	3.92	1.33	-	6.67	-	6.94	-	0.34(exo) -0.39(endo)	-
<u>5-6</u>	$\Delta\delta_{\text{H}}$ (ppm)	0.08	-0.16(exo)	-	0.27	-	-0.06	0.00	-	-
<u>9</u> ⁴	δ_{C}	34.1	26.3	-	-	144.1	123.5	125.6	-	-
<u>7</u>	δ_{C}	34.6	24.0	20.5	-	147.0	123.8	125.6	-	13.4
<u>7-9</u>	$\Delta\delta_{\text{C}}$ (ppm)	0.5	-2.3	-	-	2.9	0.3	0.0	-	-
<u>8</u>	δ_{C}	34.9	25.8	11.2	-	140.2	124.0	126.4	2.7	-
<u>8-9</u>	$\Delta\delta_{\text{C}}$ (ppm)	0.8	-0.5	-	-	-3.9	0.5	0.8	-	-
<u>2</u>	δ_{C}	34.6	7.9	19.0	-	142.9	122.9	125.7	2.2	12.8
<u>2-7</u>	$\Delta\delta_{\text{C}}$ (ppm)	0.0	-16.1	-1.5	-	-4.1	-0.9	0.1	-	-0.6
<u>2-8</u>	$\Delta\delta_{\text{C}}$ (ppm)	-0.3	-3.3	-6.8	-	2.7	-1.1	-0.7	-0.5	-
<u>3</u>	δ_{C}	36.1	14.8	-	-	136.1	124.3	126.0	7.5	-
<u>3-8</u>	$\Delta\delta_{\text{C}}$ (ppm)	1.2	-11.0	3.6	-	-4.1	0.3	-0.4	4.8	-
<u>6</u> ⁴	δ_{C}	40.2	25.8	-	134.9	144.1	122.5	124.9	-	-
<u>4</u>	δ_{C}	41.2	16.7	-	130.9	147.4	122.9	124.5	-	13.7
<u>4-6</u>	$\Delta\delta_{\text{C}}$ (ppm)	1.0	-9.1	-	-4.0	3.3	0.4	-0.4	-	-
<u>5</u> ^d										

^a ^1H NMR spectra were taken with a Varian HA-100 spectrometer at 100 MHz in CCl_4 (about 5 w/v %), accuracy of the chemical shift, δ_{H} is ± 0.01 . ^{13}C NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz in CDCl_3 containing TMS as an internal reference in 8-mm sample tubes, the accuracy of δ_{C} is about ± 0.1 .

^b The accuracy is about ± 0.02 for δ_{H} because these values are based on the first-order analyses.

^c ^{13}C signals were assigned according to G. Jikeli, W. Herrig and H. Gunther, *J. Amer. Chem. Soc.* **96**, 323 (1974).

^d Not determined.

Recently,⁷ we reported that strong steric γ -effects⁸ (upfield shift) were observed with ¹³C NMR signals due to the bridge-methylene carbon and the ethylenic carbons in *exo*- and *endo*-tricyclo[3 2 1 0^{2,4}]-octenes, respectively, as compared with those in norbornene. Similar effects, though to lesser extents, were observed in the spectra of *exo*- and *endo*-2,5-dicyanotricyclo[4 2 1 0^{2,5}]non-7-enes.⁹ Thus, in order to examine the effect of a cyclopropane ring upon ¹³C chemical shifts in a bicyclo[2 2 2]octene ring, the natural-abundance ¹³C FT NMR spectra, both ¹H noise-decoupled and single-frequency off-resonance decoupled,⁸ of the compounds described here were determined, the results are also shown in the TABLE

As a result, the objective γ -effect was found to be weak (about -2~-4 ppm) as expected from the longer distances between the cyclopropane proton and the bridge and the ring-juncture carbons which interact. An unexpected finding was that introduction of an *endo*-cyclopropane ring to skeleton 8 (from 8 to 3) causes a considerable downfield shift of cyclopropane-carbon g (+4.8 ppm), on the other hand, introduction of an *exo*-cyclopropane ring (from 8 to 2) has no significant effect upon carbon g (-0.5 ppm)

Research on similar phenomena is in progress

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