The ^<13>C NMR Chemical Shift Comparisons of Dihydrohomobarrelenones

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Abstract: The ¹³C NMR chemical shifts of various dihydrohomobarrelenones, bicyclo [3.2.2] hepta-3, 6-dien-2-ones, were compiled and compared each other. These conformationally rigid bicyclic compounds showed a good correlation on the substituent effects, which made the structure elucidations easy.

During our studies[1-5] on the high-pressure cycloaddition of tropones to a series of dienophiles, various bicyclo [3.2.2] nona-3, 6-dien-2-ones, 8, 9-dihydrohomobarrelenone derivatives, were prepared. Since these rigid bicyclic compounds possess a considerable theoretical interest, it is worthy to study their NMR spectra in detail. Herein, we record the mutually-compared ¹³C NMR chemical shift data of these derivatives.

Results and Discussion

At first, we have measured the ¹³C NMR spectrum of the parent bicyclo[3.2.2]nona-3, 6-dien-
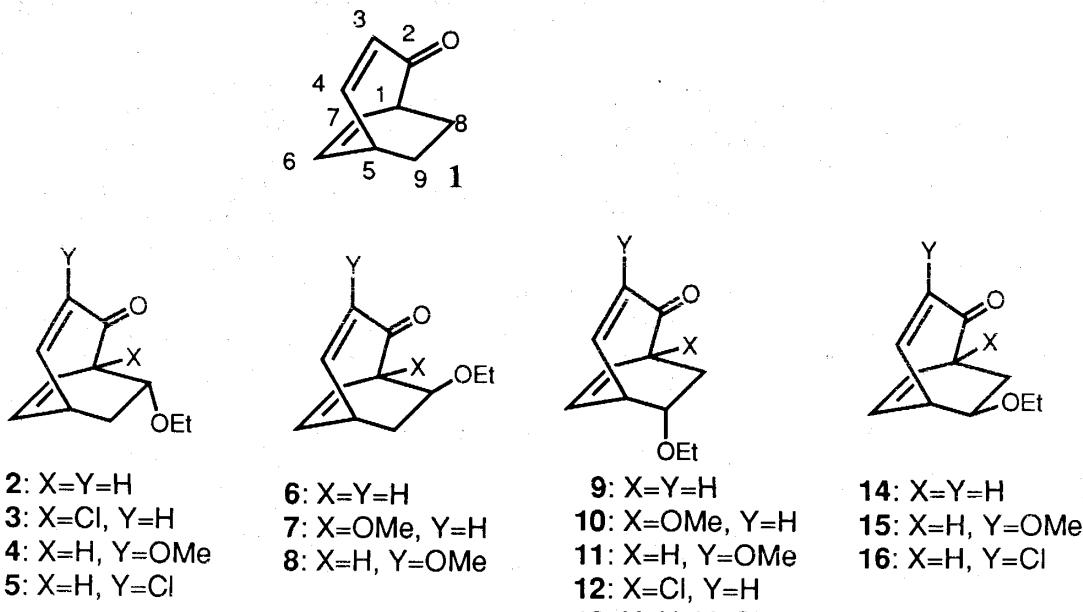
2: X=Y=H
3: X=Cl, Y=H
4: X=H, Y=OMe
5: X=H, Y=Cl

6: X=Y=H
7: X=OMe, Y=H
8: X=H, Y=OMe

9: X=Y=H
10: X=OMe, Y=H
11: X=H, Y=OMe
12: X=Cl, Y=H
13: X=H, Y=Cl

14: X=Y=H
15: X=H, Y=OMe
16: X=H, Y=Cl

Fig. 1

2-one (1)[6] [^{1}H NMRδ=1.75 (1H, m, 9α). 1.89 (1H, m, 8β), 1.97 (1H, m, 9β), 1.99 (1H, m, 8α), 3.53 (1H, tdm, J=8.4, 2.2 Hz, H-1), 3.37 (1H, dddm, J=8.4, 7.3, 0.7 Hz, H-5), 5.78 (1H, ddd, J=11.0, 2.2, 0.7 Hz, H-3), 6.06 (1H, ddm, J=8.4, 7.7 Hz, H-7), 6.54 (1H, ddm, J=8.4, 7.3 Hz, H-6), and 7.07 (1H, dd, J=11.0, 8.4 Hz, H-4). ^{13}C NMR δ=21.2 (C-8), 26.9 (C-9), 37.0 (C-5), 52.4 (C-1), 126.6 (C-7), 129.9 (C-3),138.7 (C-6), 153.4 (C-4), and 198.5 (C-2)]. The full assignment was performed by an aid of two-dimensional C-H COSY experiments and the spectral charts were illustrated in Fig. 1. The substituent effect was estimated from these standard figures as described below.

The ^{13}C NMR Chemical Shifts of the Bicyclo[3.2.2]nona-3, 6-dien-2-ones.

Recently, we have employed the ^{1}H NMR chemical shifts and coupling sequences to deduce the structures of ethoxy[3] and cyano derivatives.[4] The accurate data from the 270 MHz instrument were quite reliable, but still there is an uncertainty in order to make the first-order analysis of structures by means of coupling sequences due to occasional overlapping of proton signals. The well-separated ^{13}C NMR signals, therefore, should be more reliable for structural elucidations of the 8,9-dihydrohomobarrelenones with the rigid carbocyclic framework.

The Effect of Substituents on the C-1 and C-3 Positions of the Dihydrohomobarrelenones. We have prepared a series of 8-and 9-ethoxydihydrohomobarrelenones by condensation of ethoxyethene to tropone, 2- chlorotropone, and 2-methoxytropone. Fortunately, these tropones afforded more than three [4+2] cycloadducts, and four 8α-, three 8β-, five 9α-, and three 9β-ethoxydihydrohomobarrelenones were obtained. This made possible to check an effect from C-8 and C-9 substituents of dihydrocomobarrelenones. The data are compiled in Table 1.

From the table, it is recognizable that within the families classified by positions and orienta-
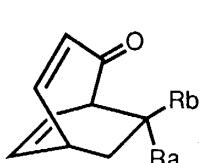

17: Ra=CN, Rb=H
18: Ra=H, Rb=CN
21: Ra=Ph, Rb=H
22: Ra=Ph, Rb=Me
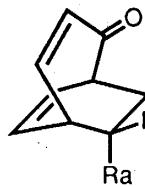
19: Ra=CN, Rb=H
20: Ra=H, Rb=CN
23: Ra=Ph, Rb=H
24: Ra=Ph, Rb=Me
25: Ra=H, Rb=Ph
26: Ra=Me, Rb=Ph

Chart 1

Table 1. The ^{13}C NMR Chemical Shift Comparisons of Ethoxybicyclo[3.2.2]nonadienes

| No. | 8α-Ethoxy Derivatives | | | | No. | 8β-Ethoxy Derivatives | | |
	2 H	3 1-Cl	4 3-MeO	5 3-Cl		6 H	7 1-MeO	8 3-MeO
C - 1	58.9	83.9(+25.0)*	57.8(−1.1)	57.7(−1.2)	C - 1	57.7	92.5(+34.8)*	56.6(−1.1)
C - 2	195.7	187.7(−8.0)	191.3(−4.4)	188.4(−7.3)	C - 2	195.7	192.5(−3.2)	191.3(−4.4)
C - 3	129.4	131.9(+2.5)	150.4(+21.0)*	132.0(+2.6)*	C - 3	131.0	130.0(−1.0)	152.3(+21.3)*
C - 4	153.9	154.3(+0.4)	120.3(−33.6)	150.0(−3.9)	C - 4	153.5	150.9(−2.6)	120.3(−33.2)
C - 5	35.5	35.4(−0.1)	35.7(+0.2)	34.9(−0.6)	C - 5	36.7	36.3(−0.4)	36.6(−0.1)
C - 6	138.4	135.7(−2.7)	139.8(+1.4)	138.3(−0.1)	C - 6	139.8	138.0(−1.8)	140.6(+0.8)
C - 7	124.8	127.2(+2.4)	124.0(−0.8)	124.9(+0.1)	C - 7	125.3	128.8(+3.5)	124.6(−0.7)
C - 8	75.7	78.6(+2.9)	75.6(−0.1)	75.1(−0.6)	C - 8	75.1	78.5(+3.4)	74.9(−0.2)
C - 9	34.8	33.7(−1.2)	32.0(−2.8)	34.9(+0.1)	C - 9	36.4	34.9(−1.5)	33.6(−2.8)

Table 1. Contn'd

No.	9α-Ethoxy Derivatives					No.	9β-Ethoxy Derivatives		
	9 H	**10** 1-MeO	**11** 3-MeO	**12** 1-Cl	**13** 3-Cl		**14** H	**15** 3-MeO	**16** 3-Cl
C-1	51.1	85.7(+34.6)*	50.3(-0.8)	83.6(+32.5)*	50.1 (-1.0)	C-1	51.7	50.5(-1.2)	50.6(-1.1)
C-2	197.3	194.5(-2.8)	192.9(-4.4)	188.0(-9.3)	190.0(-7.3)	C-2	197.6	193.3(-4.3)	190.4(-7.2)
C-3	130.9	130.9(0.0)	151.5(+20.6)*	133.4(+2.5)	133.3(+2.4)*	C-3	131.0	151.5(+20.5)*	133.1(+2.1)*
C-4	149.2	147.8(-1.4)	115.8(-33.4)	148.6(-0.6)	145.5(-3.7)	C+4	149.5	115.3(-34.2)	146.2(-3.3)
C-5	42.1	41.8(-0.3)	39.0(-3.1)	42.4(+0.3)	41.8 (-0.3)	C-5	41.9	38.9(-3.0)	42.0(+0.1)
C-6	135.1	133.6(-1.5)	136.5(+1.4)	134.1(-1.0)	135.2(+0.1)	C-6	136.5	137.9(+1.4)	136.5(0.0)
C-7	127.6	129.4(+1.8)	127.0(-0.6)	128.9(+1.3)	127.6(0.0)	C-7	127.2	126.5(-0.7)	127.2(0.0)
C-8	30.7	35.5(+4.8)	30.4(-0.3)	41.1(+10.4)	30.2 (-0.5)	C-8	28.6	28.1(-0.5)	28.1(-0.5)
C-9	77.8	75.2(-2.6)	78.2(+0.4)	76.2(-1.6)	77.1 (-0.7)	C-9	79.5	78.4(-1.1)	78.9(-0.6)

tions of ethoxy group, only the vicinity of the substituents from the tropone moieties showed large differences in chemical shifts. Therefore, the chemical shift comparisons provide informations to deduce positions and orientations of substituents.

Electronic and Steric Effects of Substituents on C-8 and C-9 of Dihydrohomobarrelenones. In addition to above ethoxy derivatives of dihydrohomobarrelenones, we prepared cyano derivatives from tropone with acrylonitrile[4]. Since ethoxy group is an electron-releasing and cyano group in strongly electron-withdrawing, the comparison of chemical shifts from the both derivatives will enable to evaluate an electronic effect of ^{13}C chemical shifts. Mutual comparisons of 8- and 9-ethoxy and cyano derivatives in the same families are illustrated in Table 2.

Again, as could be seen in Table 2, only proximity of the substituents caused considerable chemical shift diffemences; other than the $\Delta \delta$ for the carbons bearing the substituents, ca. 50, the $\Delta \delta$ were very small. However, the subtle difference could be used for assignment of the carbons and structure determination. For examples, in 8-substituted derivatives, the $\Delta \delta$ for C-1 were -3.4 and -3.2, but those of C-5, the other bridge- head carbon, were +0.1 and -1.0. The reverse were also true in 9-substituted derivatives; the $\Delta \delta$ for C-5 were -2.7 and -3.0 and the $\Delta \delta$ for C-1 were -0.1 and -0.8. Moreover, the $\Delta \delta$ of C-6 or C-7 were larged for 8α- and 9β-derivatives. This should mean that electronic effect of any substituents on the sp^3-carbons may not obscure the ^{13}C NMR chemical shift assignment.

Therefore, the chemical shift informations are quite reliable to determine the structures.

The Spectral Comparisons of the 9- and 8-Phenyldihydrohomobarrelenones vs 9-Phenyl-9-methyl- and 8-Phenyl-8-methyldihydrocomobarrelenones. By means of high-pressure cycloaddition procedure, we could synthesize Diels-Alder adducts from α-methylstyrene with tropone, the combination of which gave no reaction products under atmospheric pressure. Their ^{1}H NMR spectra showed some anomalies on the chemical shifts due to mobile conformations of phenyl group. Therefore, the structure elucidations were depended on mostly analyses of coupling sequences and extensive NOE measurements. Apart from the structure analysis, comparisons of the ^{13}C NMR are worthy of note since the steric environment of these adducts are considerably different. As could

Table 2. The Mutual ^{13}C NMR Chemical Shift Comparisons of Ethoxybicyclo[3.2.2]-nonadienones and Cyanobicyclo[3.2.2]nonadien-2-ones

No.	8-Substituted Derixatives			9-Substituted Derivatives		
	8α-OEt 2	8β-OEt 16	Δδ$_{(α-β)}$	9α-OEt 9	9β-OEt 14	Δδ$_{(α-β)}$
C − 1	58.9	57.7	+1.2	51.1	51.7	−0.6
C − 2	195.7	195.7	0	197.3	197.6	−0.3
C − 3	129.4	131.0	−0.6	30.9	131.0	−0.1
C − 4	153.9	153.5	+0.4	149.2	149.6	−0.5
C − 5	35.5	36.7	−1.2	42.1	41.9	+0.3
C − 6	138.4	139.8	−1.4	135.1	136.5	−1.4
C − 7	124.8	125.3	−0.5	127.6	127.2	+0.4
C − 8	75.7	75.1	+0.6	30.7	28.6	+2.1
C − 9	34.8	36.4	−1.6	77.8	79.5	−1.7
No.	8α−CN 17	8β−CN 18	Δδ$_{α-β}$	9α−CN 19	9β−CN 20	Δδ$_{α-β}$
1	55.1	54.5	+0.6	51.0	50.9	+0.1
2	195.8	193.5	+2.3	195.7	195.8	−0.1
3	129.8	130.6	−0.8	131.4	132.1	−0.7
4	152.3	152.6	−0.3	148.3	147.5	+0.8
5	35.6	35.7	−0.1	39.4	38.9	+0.5
6	140.1	139.5	+0.6	135.6	137.0	−1.4
7	124.3	125.3	−1.0	128.5	127.2	+1.3
8	24.3	24.4	−0.1	26.8	25.9	+0.9
9	32.6	32.3	+0.3	29.1	29.7	−0.6

Table 3. The ^{13}C NMR Chemical Shift Comparisons of Cyano- and Ethoxybicyclo-[3.2.2]nonadienones

No.	8α−CN 17	8α−EtO 2	Δδ$_{(CN-EtO)}$	8β−CN 18	8β−EtO 6	Δδ$_{(CN-EtO)}$
1	55.1	58.5	−3.4	54.5	57.7	−3.2
2	195.8	195.7	+0.1	193.5	195.7	−2.2
3	129.8	129.4	+0.4	130.6	131.0	−0.4
4	152.3	153.9	−1.6	152.6	153.5	−0.9
5	35.6	35.5	+0.1	35.7	36.7	−1.0
6	140.1	138.4	+1.7	139.5	139.8	−0.3
7	124.3	124.8	−0.5	125.3	125.3	0.0
8	24.3	75.7	−51.4	24.4	75.1	−50.7
9	32.6	34.8	−2.2	32.3	36.4	−4.1
No.	9α−CN 19	9α−EtO 9	Δδ$_{(CN-EtO)}$	9β−CN 20	9β−EtO 14	Δδ$_{(CN-EtO)}$
1	51.0	51.1	−0.1	50.9	51.7	−0.8
2	195.7	197.3	−1.6	195.8	197.6	−1.8
3	131.4	130.9	+0.5	132.1	131.0	+1.1
4	148.3	149.2	−0.9	147.5	149.6	−2.1
5	39.4	42.1	−2.7	38.9	41.9	−3.0
6	135.6	135.1	+0.5	137.0	136.5	+0.5
7	128.5	127.6	+0.9	127.2	127.2	0.0
8	26.8	30.7	−3.9	25.9	28.6	−2.7
9	29.1	77.8	−48.7	29.7	79.5	−49.8

Table 4. The ^{13}C NMR Chemical Shift Comparisons of 8- and 9-Phenyl bicyclo[3.2.2]nona-3,6-dien-2-ones in CDCl$_3$

	C − 1	C − 2	C − 3	C − 4	C − 5	C − 6	C − 7	C − 8	C − 9	Subst.
21	59.9	196.9	129.5	152.4	40.0	140.4	125.0	37.2	36.7	8α−Ph
22	64.8	197.8	130.0	153.7	41.8	137.4	125.9	41.8	37.0	8α−Ph−8β−Me
Δδ	−4.9	−0.9	−0.5	−1.3	−1.8	+3.0	−0.9	−4.6	−0.3	
23	53.2	198.1	129.8	154.4	45.5	136.0	129.2	31.3	44.4	9α−Ph
24	52.1	197.7	130.3	152.0	48.7	139.4	125.1	35.9	46.7	9α−Ph−9β−Me
Δδ	+1.1	+0.4	−0.5	+2.4	−3.2	−3.4	+4.1	−4.6	−2.3	
25	52.3	198.2	130.9	150.7	46.5	140.6	125.5	28.4	45.0	9β−Ph
26	52.7	197.7	128.9	152.8	47.7	138.5	125.9	35.6	47.6	9β−Ph−9α-Me
Δδ	−0.4	+0.5	+2.0	−2.1	−1.2	+2.1	−0.4	−7.2	−2.6	

be seen in Table 3, again large differences were observed in the vicinity of the substituents. Since, in view of a presence of quaternary carbon, the first-order analysis of the ^{1}H NMR spectra with the adducts derived from α-methylstyrene did not provide reliable information, this ^{13}C NMR data were quite useful.

The ^{13}C NMR Chemical Shifts of the Diels-Alder Adducts of Tropones to 2,3-Bis(methoxy-carbonyl)-7-oxanorbornadiene. In addition to above mentioned compounds, we have synthesized


27: X=Y=H	**33**: X=Cl, Y=H
28: X=OH, Y=H	**34**: X=H, Y=Cl
29: X=Cl, Y=H	**35**: X=H, Y=OMe
30: X=H, Y=Cl	**36**: X=OMe, Y=H
31: X=OMe, Y=H	
32: X=H, Y=OMe	

Chart 2
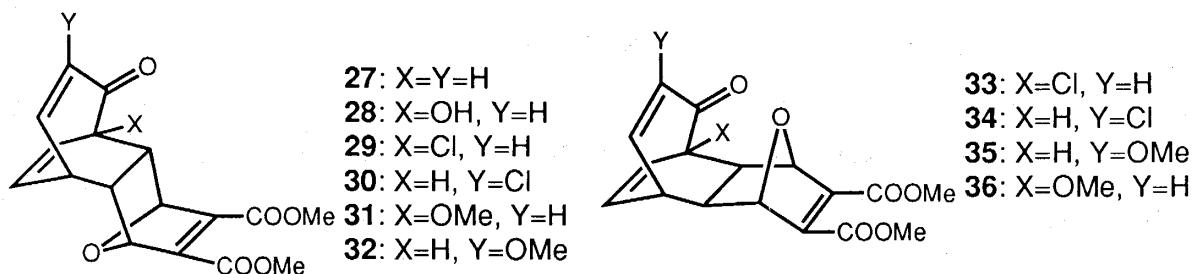
Table 5. The ^{13}C NMR Chemical Shifts of Dihydrohomobarrelenone Moiety of 2,3-Bis(methoxy-carbonyl)-7-Oxanorbornadiene Adducts of Tropones in CDCl$_3$.

	C − 1	C − 2	C − 3	C − 4	C − 5	C − 6	C − 7	C − 8	C − 9
1	52.4	198.5	129.9	153.4	37.0	138.7	126.6	21.2	26.9
27	48.2	196.3	129.5	153.7	39.7	136.1	126.8	41.8	48.2
28	*82.1*	a)195.3	132.6	155.8	39.7	133.8	125.7	46.3	49.1
29	*81.1*	187.7	132.5	153.8	38.8	135.0	127.7	48.9	49.8
30	47.8	189.0	*132.7*	150.0	39.5	136.1	127.0	41.5	47.8
31	*83.5*	195.1	133.5	152.8	39.7	133.5	128.6	45.8	47.1
32	48.8	191.8	*151.1*	120.8	36.7	137.6	126.2	41.7	48.8
33	*83.6*	187.0	136.3	146.8	37.3	138.3	132.8	45.6	57.4
34	54.9	189.7	*136.4*	145.8	38.0	139.6	129.9	46.0	46.8
35	55.1	192.3	*154.9*	114.0	35.1	141.0	129.0	45.4	46.9
36	*83.2*	193.2	133.5	146.4	38.0	144.8	132.3	44.2	52.5

a) Italic figures are chemical shifts of carbons bearing substituents.

various types of derivatives to date.   Among them, we like to add the data of series of Diels-Alder adducts of tropones .to 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene, which served as immediate precursors to furnish homobarrelenone dirivatives.[1)]   Their chemical shift data were compiled in Table 5 to show a close resemblance according to their structural types.

Conclusion.   Throughout the table, the ^{13}C chemical shifts are mutually consistent, and this conformationlally rigid bicyclic compounds will serve as good model compounds for the NMR analysis of related derivatives[7)].

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和 文 概 要

8，9 - ジヒドロホモバーレレノン誘導体はトランスアニュラーコンジュゲーションを示す興味ある双環状化合物である。その[13]C NMR の化学シフトは構造解析に非常に有用な情報を与えた。本報告では関連化合物の構造解析に有効なそれら化学シフトに及ぼす置換基効果を整理して表示した。