The ^{13}C-NMR Assignment of Some Spirocyclopropane-attached Derivatives of the Dicyclopentadiene by the Epoxidation Shift

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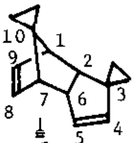
The ^{13}C-NMR assignment of dispiro[cyclopropane-1,3'-tricyclo[5.2.1.0^{2,6}]-deca-4',8'-diene-10',1"-cyclopropane] and its derivatives was given by the comparison of the magnitudes of the residual coupling in the off-resonance spectra and by the chemical shift differences induced by the epoxidation of a double bonds. This was in accord with the former assignment for the dicyclopentadiene by Nakagawa *et al.*

The ^{13}C-NMR spectroscopy is a powerful mean of organic structure analysis, but the assignment of the spectra is often difficult in complicated systems. During the photooxidations of dispiro[cyclopropane-1,3'-tricyclo[5.2.1.0^{2,6}]deca-4',8'-diene-10',1"-cyclopropane](1),[1] the Diels-Alder dimer of spiroheptadiene(A), we have measured a number of the ^{13}C-NMR spectra of derivatives. Since they are rigid cage compounds, the full analysis of the spectra should provide an intimate information for analyzing ^{13}C-NMR spectra of similar alicyclic derivatives. Indeed, this was the case when the assignment of the spectra of 1 and its derivatives, obtained by mutual comparison, made a selection of the previous NMR assignments[2,3] for some derivatives of the *endo*-dimer(27) of cyclopentadiene(B), a basic cage compound.



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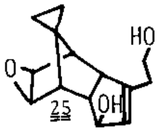

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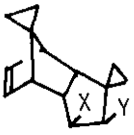

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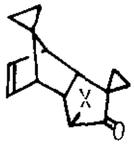
3:X,Y=-O-O-
4:X,Y=-O-CH$_2$O-
5:X=Y=OH
6:X=OH, Y=OCOPh
7:X=OCOPh, Y=OH
8:X=Y=OCOPh

19:X=Y=OH
20:X=OH, Y=OCOAr*
21:X=OH, Y=OMe
22:X=OMe, Y=OH
23:X=Y=OMe
(*Ar=m-Cl-C$_6$H$_4$-)



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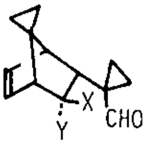
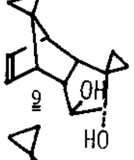


13:X=H, Y=CHO
14:X=CHO, Y=H



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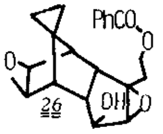

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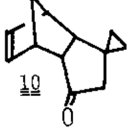

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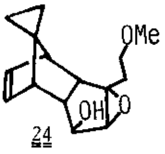

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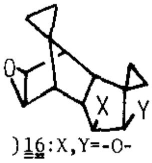
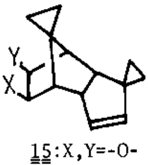


16:X,Y=-O-
17:X=Y=OH



15:X,Y=-O-
18:X=Y=OH

Table 1: The ^{13}C-NMR Spectra of 1 and its Derivatives (in $CDCl_3$).

	C-1+C-7		C-2	C-6	C-8+C-9		C-4	C-5	C-3	C-10	C-3α+β	C-10s+a
1[a]	*50.6*[b]	*51.6*	*49.8*	*55.4*	*134.2*	*133.3*	140.4	129.1	29.7	45.4	11.5, 15.4	5.7, 7.5
2	51.1*[c]	52.0*	52.4*	49.7	136.0	133.2	69.0[d]	61.1	25.1	46.1	10.5, 11.2	5.4, 7.6
3	49.9	51.9	57.2*	58.1*	138.3	133.2	98.4	90.0	30.0	46.4	11.3, 15.3	5.9, 7.9
4	50.8	52.3*	51.8*	56.9*	137.9	134.2	87.2	83.3	25.3	45.5	11.7, 12.9	5.7, 7.8
5	50.8*	52.5	50.2*	53.9	137.5	135.1	79.8	74.7	25.8	47.2	8.9, 9.9	5.8, 8.0
6	49.9	51.9*	50.4*	54.4	137.1	135.4	84.7	74.1	24.6	47.8	10.2, 10.2	5.8, 7.9
7	50.2	51.6*	50.6*	52.2	137.4	135.4	78.1	79.2	26.3	47.4	9.3, 9.3	5.8, 7.9
8	50.1*	52.1*	50.1*	52.3*	137.0	135.8	83.0	75.8	24.9	47.9	9.8, 11.1	5.9, 8.0
9	48.9*	49.0*	49.8*	49.9*	136.9	135.3	80.6	78.9	23.7	47.7	8.0*, 8.9	5.9, 7.8*
10	50.7	51.7*	52.6*	57.5	136.0	134.4	51.5	220.2	18.4	46.8	10.4, 19.1	6.0, 8.0
11	50.4	52.1*	51.6*	38.3	137.1	134.4	219.8	40.3	31.4	44.7	15.9, 23.6	5.4, 7.4
12	50.0*	51.0*	51.0*	48.0	137.2	135.5	215.0	77.2	31.5	45.8	19.6, 23.3	5.7, 7.6
13	41.8	49.8	50.7	57.3	137.2	133.5	204.2	201.6	33.3	45.9	11.2, 12.5	6.3, 8.3
14	39.6	50.6	51.5	56.6	135.8	135.8	203.3	201.4	33.3	44.7	9.9, 10.4	5.5, 8.9
15	*46.4*	*45.8*	*50.0*	*53.3*	*52.6*	*51.4*	*140.0*	*127.6*	27.6*	27.9*	12.0, 15.6	0.5, 8.8
16	46.7	46.0	52.2	48.7	51.1	50.4	68.2	59.6	22.7	27.6	10.9, 11.6	0.5, 9.0
17	45.8*	46.6*	50.0	52.4	52.0	50.8	77.2	73.2	23.6	27.1	7.1, 11.0	0.6, 9.2
18	52.0*	51.1*	48.1	52.2*	72.9	72.2	138.7	128.7	28.0	33.0	10.8, 15.2	0.2, 6.3
19	49.2	49.9*	56.1	54.0	133.1*	134.4*	130.8	77.8	147.0	47.0	33.3, 59.8	5.8, 7.6
20	49.2*	49.9*	56.7	54.1	132.9*	134.3*	130.4	77.9	146.2	47.0	29.5, 63.3	5.8, 7.5
21	49.3*	49.9*	56.6	54.1	133.1*	134.4*	130.0	77.7	146.8	46.9	30.4, 70.6	5.8, 7.5
22	49.2*	50.2*	56.7	50.4	133.1*	134.6*	127.4	87.1	148.2	47.2	33.6, 60.1	5.8, 7.6
23	49.38	50.4*	57.1	50.4	133.2*	134.6*	126.8	87.1	148.3	47.1	30.6, 70.8	5.8, 7.6
24	49.8*	50.1*	53.6*	54.4*	134.7*	135.5*	69.2	74.5	69.7	47.1	30.4, 68.6	5.6, 7.7
25	43.4*	45.3*	54.3*	53.4*	50.5*	51.4*	130.8	75.3	145.4	28.4	33.6, 59.6	0.5, 9.2
26	45.5*	45.7*	51.0	53.9	50.6*	49.9*	69.8	70.9	68.0	28.2	30.1, 61.5	0.6, 9.4

a) For preparation of 1-26, see Ref. 1.
b) Figures expressed in italic letters were determined by selective decoupling experiments.
c) Asterisked figures may be mutually reversed.
d) Underlined figures were assigned by magnitudes of J_R in the off-resonance experiments.

First of all, among eight methine carbon signals of a bisepoxide(16) appearing in a range of 45 to 70 ppm from internal TMS, the two at δ: 68.2 and 59.6, being deshielded than others, are ascribable to the oxygenated carbons(C-4 and C-5) by comparisons with the 4,5-epoxide of 1(2). The others appearing together in narrow range, 46 to 52 ppm, are difficult to make a clear assignment on the chemical shift ground, but the large residual coupling in the off-resonance spectrum(J_R) for the signals at 50.4 and 51.1 (each 66 Hz)[4] led to assign them to be C-9 and C-8 from others (*ca.* 48 Hz). Same is true for 8,9-epoxide(15) of 1: Among six methine carbons appeared between 46 to 53, the epoxy carbon signals were shown to be at 52.6(C-8) and 51.4(C-9) by larger J_R(*ca.* 60 and 64 Hz), than the others(40 to 43 Hz). Similarly, a diepoxy glycol monoester(**26**) showed two methine carbons at *ca*. 70 ppm; one at 70.9 is attributable to the *hydroxyl carbon, and the other at* 69.8 having large J_R to C-4 epoxy signal. The remaining epoxy carbon signals were at 49.9 and 50.6. An epoxy alcohol(**25**) revealed a similar feature.

Nextly, α-carbons of aldehydes were also assignable; the spectrum of **13** showed such signals, C-3 and C-6, with large $^{2}J_{CC-H}$-splittings at 33.3(d, J_R=14 Hz) and 57.3 (dd, J_R=48, 10 Hz). The whole data are compiled in Table 1.

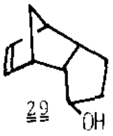
Based on the above assignment, we have tried a differentiation of previous ^{13}C-NMR assignments2,3) on **27** and its derivatives by comparisons of the Δδ induced by the epoxidation, since we have a series of epoxy derivatives for comparison. Indeed, the 8,9-epoxidation caused a remarkable change in their carbon chemical shifts. As expected, the Δδ for C-8 and C-9 were as large as -80 to -86 ppm, which are similar to that of the epoxidation shift between **29** and its 8,9-epoxy derivative(**30**), Δδ(**30**-**29**), -85.2, but, our Δδ for the C-10 were *ca*. -17 to -20, being smaller than that of Δδ(**30**-**29**), -22.7. This must be due to the proximity of the epoxy to spirocyclopropane groups. Contrasting figures observed for the epoxidation shifts of C-10a(*ca*. -5) and C-10s(*ca*. +1.5) in these derivatives must be interpreted on the same ground, and constituted a firm evidence for differentiation of C-10 and C-3 *methylene carbons*. As figured in Table 2, our Δδ of methine carbons were consistent to the data of norbornene series,5) and in the same time, the whole Δδ(**30**-**29**) *data disproved* the Kleinpeter's assignment.3)

Table 2: The Chemical Shift Differences due to the Epoxidation at C-8 and C-9.

Δδ	C-1	C-7	C-2	C-6	C-8	C-9	C-3	C-10	C-10s	C-10a	C-3α	C-3β
(**15**-**1**)	-4.2	-5.8	+0.2	-2.1	-81.6	-81.9	-2.1	-17.5	+1.3	-5.2	+0.5	+0.3
(**16**-**2**)	-4.4	-6.0	-0.2	-1.0	-84.9	-82.8	-2.4	-18.5	+1.4	-4.9	+0.4	+0.4
(**17**-**5**)	-5.0	-5.9	-0.2	-1.5	-85.5	-84.3	-2.3	-20.1	+1.2	-5.2	-1.6	+1.1
(**25**-**19**)	-5.8	-4.6	-1.8	-0.6	-82.6	-83.0	-1.6	-18.6	+1.6	-5.3		
(**26**-**24**)	-4.3	-4.4	-2.6	-0.5	-84.8	-84.9	-1.7	-18.9	+1.7	-5.0		
(**30**-**29**)a)	-5.4	-5.7	-0.3	-1.5	-85.2	-85.2	-2.2	-22.7				
(**30**-**29**)b)	-0.3	-5.8	-5.7	-1.5	-85.2	-85.2	-2.2	-22.7				

a) Calculated after revision of the data given in Ref. 3.
b) Calculated after assignment of Ref. 3.

On the other hand, the Nakagawa's assignment showed a consistency with our results; using their figures of **27** and **28**,2) *Δδ(**1**-**27**) and Δδ(**19**-**28**) were calculated*. Relatively large Δδ(**1**-**27**) values observed were all explained in terms of the spirocyclopropanes; C-a, C-g, C-b and C d showed a down-field shift, while C-c and C-k,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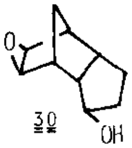
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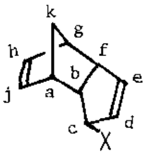
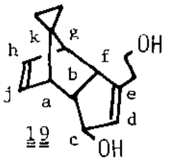


27:X=H
28:X=OH



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spirocarbons, did a high-field shift. The Δδ(1-27) of C-d and C-e showed same signs and order in magnitudes with the Δδ(A-B) of the α- and β-carbon signals(+7.0 and -3.7). The Δδ(19-28) were also characteristic; especially, by removing one of the spirocyclopropane rings, the down-field shift for C-b and C-d and the high-field shift for C-c disappeared. Large negative Δδ, -6.3 for C-d, and positive Δδ, +11.8 for C-e, are ascribable to a newly formed β-hydroxyethyl group at C-e; the figures coincide well with those of cyclopentene and its 1-propyl derivative (-6.7 and +13.7)

Table 3. The ^{13}C-NMR Comparisons of 1 and 19 with 27 and 28.

	C-a	C-g	C-b	C-f	C-h	C-j	C-d	C-e	C-c	C-k
1	50.6	51.6	49.8	55.4	134.2	133.3	140.4	129.1	29.7	45.4
27[a]	46.3	45.3	41.3	54.8	131.9	132.2	132.1	135.6	34.7	50.3
Δδ	+4.3	+6.3	+8.5	+0.6	+2.3	+1.1	+8.3	-6.5	-5.0	-4.9
19	49.9	49.2	54.0	56.1	134.4	133.1	130.8	147.0	77.8	47.0
28[a]	44.5	44.5	53.0	54.5	132.2	134.6	137.1	135.2	78.4	51.1
Δδ	+5.4	+4.7	+1.0	+1.3	+2.2	-1.5	-6.3	+11.8	-0.6	-4.1

a) Data were taken from Ref. 2.

References and Notes

†) This paper is dedicated to Prof. Tetsuji Kametani, Tohoku University.

1) H. Takeshita and T. Hatsui, *J. Org. Chem.*, 1978, 43, 3080; H. Takeshita, T. Hatsui, and H. Mametsuka, *Heterocycles*, 1978, 11, 323; T. Hatsui and H. Takeshita, *Bull. Chem. Soc. Jpn.*, 1980, 53, 2027; T. Hatsui and H. Takeshita, *Bull. Chem. Soc. Jpn.*, 1980, 53, 2655.

2) K. Nakagawa, S. Iwase, Y. Ishii, S. Hamanaka, M. Ogawa, *Bull. Chem. Soc. Jpn.*, 1977, 50, 2391.

3) E. Kleinpeter, H. Kuhn, M. Muhlstadt, *Org. Magnetic Resonance*, 1977, 9, 312.

4) In the heteronuclear off-resonance spectra, the residual splitting (J_R) is given by Eq. 1:[6]

$$J_R=[(\Delta\nu - J_o/2)^2 + (\gamma H_2)^2]^{1/2} - [(\Delta\nu + J_o/2)^2 + (\gamma H_2)^2]^{1/2} \quad \text{... (Eq. 1)}$$

Where $\Delta\nu$ is the difference between the resonance frequencies, and γH_2 is the power of decoupling field. If $\gamma H_2 >> |\Delta\nu|$, Eq. 1 can be simplified to Eq. 2:

$$\Delta\nu=\gamma H_2 J_R/J_o \quad \text{...(Eq. 2).}$$

Hence, under certain conditions, if $\Delta\nu$ of some nuclei were nearly equal, the J_R becomes parallel to J_o, *i.e.*, to *s*-charactor.

5) D. Zimmermann, J. Reisse, J. Coste, F. Planat, and H. Cristol, *Org. Magnetic Resonance*, 1974, 6, 492.

6) K. G. R. Pachler, *J. Magnetic Resonance*, 1972, 7, 442.

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