

NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS. VII.<sup>1)</sup>

<sup>13</sup>C NMR SPECTRA OF BARBARALONE AND ITS DEGENERATE COPE REARRANGEMENT

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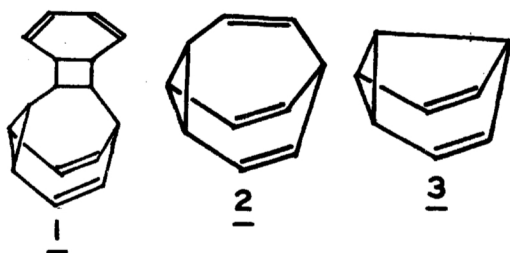
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<sup>13</sup>C NMR spectra of barbaralone were measured at several temperatures. Spin-lattice relaxation times and nuclear Overhauser enhancement factors were also determined. Complete line shape analyses of <sup>13</sup>C spectra were made by the simulation method to obtain the accurate activation parameters of the Cope rearrangement of barbaralone.

<sup>13</sup>C NMR spectroscopy is a powerful tool for the analyses of exchanging phenomena in organic molecules because of its simpler line shape than that in <sup>1</sup>H NMR. However, <sup>13</sup>C dynamic NMR spectroscopy has been used relatively rarely for this purpose.<sup>1-6)</sup> On this point of view, several studies have been made on the analyses of various thermal rearrangement of bridged 3,4-homotropylidene derivatives 1-3.<sup>3-6)</sup> Barbaralone (4) contains an sp<sub>2</sub> carbon at the bridge position and is expected to have a different activation energy in its Cope rearrangement comparing with those of structurally analogous compounds 1-3. It is worthwhile obtaining the accurate activation parameters of the rearrangement of 4, although it has been investigated using approximate <sup>1</sup>H NMR methods because of its very complex spectral patterns.<sup>7-8)</sup>

<sup>13</sup>C spectra of 4<sup>9)</sup> consists of only four peaks for the nine carbons at ambient temperature. This indicates that the Cope rearrangement of 4 occurs very rapidly at the temperature. In order to make the spectral assignment, the temperature was fully decreased (Fig.1). <sup>13</sup>C spectrum at -90.6°C is almost the same as those at -99.8 and -105.9°C. This fact shows that the rearrangement of 4 is sufficiently slow at these temperatures. The exchanging pairs of carbons in the rearrangement



process are as follows (Fig.2):  $C_1 \rightleftharpoons C_6$ ,  $C_2 \rightleftharpoons C_4$ ,  $C_5 \rightleftharpoons C_8$ .  $C_3, C_7$ , and  $C_9$  remain unchanged. Taking accounts of the numbers of carbon atoms, the aspect of temperature-dependent spectra (Fig.1), and the well

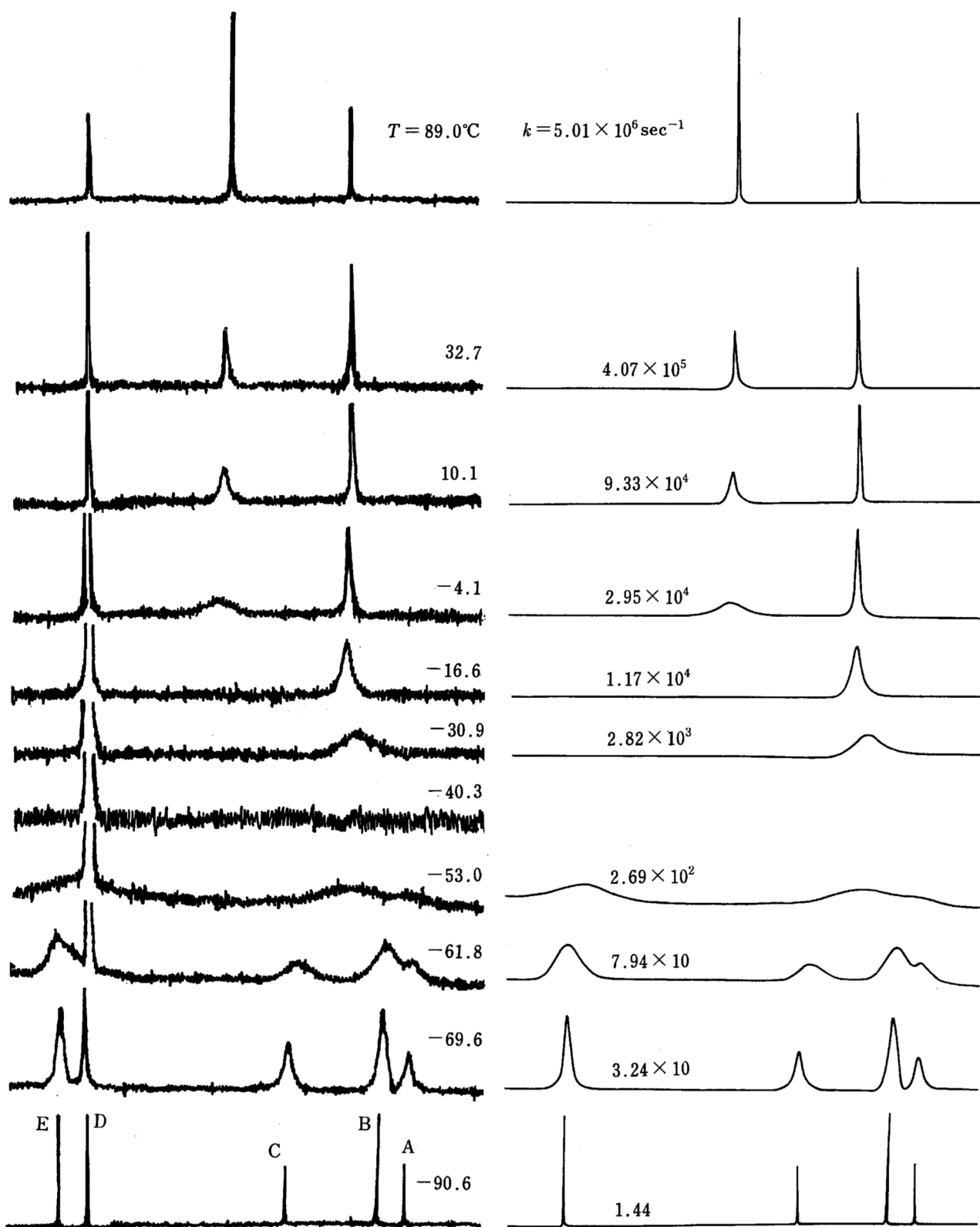


Fig.1. The observed (left) and the calculated (right) spectra of methine carbons of barbaralone at several temperatures. (The peaks of nonexchanging carbons, D, are not included in the calculated spectra.)

Table 1. Chemical shifts of  $^{13}\text{C}$  spectrum of 4 at  $-90.6^\circ\text{C}$  (from TMS)

Peak	A	B	C	D	E	carbonyl
Carbon	8	1,2	5	3,7	4,6	9
$\delta(\text{ppm})$	26.92	33.36	50.60	122.45	128.96	199.07

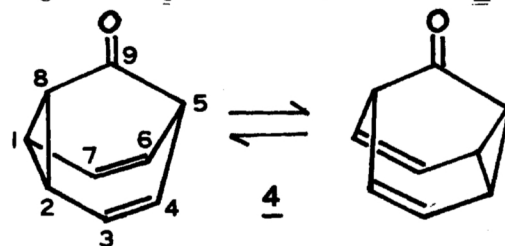
known chemical shift tendency, the assignment of the peaks in the spectrum at  $-90.6^\circ\text{C}$  was made as in Table 1.

To make a strict line shape analysis of  $^1\text{H}$  decoupled  $^{13}\text{C}$  NMR spectra, it is, of course, necessary to obtain the genuine  $^{13}\text{C}$  spectrum at each temperature, because differences in spin-lattice relaxation times ( $T_1$ ) and nuclear Overhauser enhancement factors between pairs of exchanging carbons can produce serious errors in the quantitative analyses by means of  $^{13}\text{C}$  NMR. Thus,  $T_1$ 's and NOE factors of 4 were measured at several temperatures. The results are given in Table 2. It is evident that  $T_1$ 's are not so much different from each other between carbons with a hydrogen in 4 within experimental errors. This means that almost isotropic tumbling motion occurs in this molecule. Taking accounts of these  $T_1$ 's, the pulse delay times in the measurement of  $^{13}\text{C}$  spectra were set sufficiently longer at all temperatures. The NOE factors at  $-88.6^\circ\text{C}$ , at which temperature the rearrangement occurs considerably slowly, show that eight carbons bearing one hydrogen atom relax predominantly by the dipole-dipole mechanism and that the exchanging paired peaks, A and C as well as B and E, have almost the same NOE values within experimental errors ( $\pm 0.2$ ). At  $26.7^\circ\text{C}$ , all NOE's are smaller than those at  $-88.6^\circ\text{C}$  because of some contribution of the spin-rotation mechanism. At this temperature the NOE factors of a non-exchanging peak D is not so much different from those of coalesced peaks A-C and B-E. This is also seen at  $-88.6^\circ\text{C}$ . These facts seem to indicate that in 4 the differences in NOE factors between the exchanging paired carbons are negligibly

Table 2.  $T_1$  and NOE factors of  $^{13}\text{C}$  NMR signals of 4 at several temperatures. (\*value of the coalesced peak)

	Peak $T^\circ\text{C}$	A	B	C	D	E
$T_1$	-94.8	0.13	0.13	0.15	0.12	0.14
	-81.9	0.40	0.33	0.43	0.36	0.40
	30.7	10.3*	9.0*	10.3*	6.8	9.0*
NOE	-88.6	3.0	2.9	3.0	2.8	2.8
	26.7	2.6*	2.8*	2.6*	2.5	2.8*

small. Indeed, we have not encountered any difficulty in fitting the calculated spectra to the

Fig. 2. Cope rearrangement of 4.

observed arising from the difference in  $T_1$  or NOE factors.

The complete line shape analyses of  $^{13}\text{C}$  spectra of 4 were performed for two pairs of peak A-C and B-E independently at 32 temperatures. The agreement between the experimental and theoretical spectra is excellent (Fig.1). The rate constants obtained in two analyses are in good agreement with each other in all temperatures. The activation parameters determined from Arrhenius plot and Eyring's equation are as follows;  $E_a$ :  $11.5 \pm 0.1$  Kcal/mole,  $\Delta G^\ddagger$ :  $10.1 \pm 0.1$  Kcal/mole,  $\Delta H^\ddagger$ :  $10.9 \pm 0.1$  Kcal/mole,  $\Delta S^\ddagger$ :  $2.7 \pm 0.7$  e.u. at  $25.0^\circ\text{C}$ .

$E_a$  of 4 was reported to be 8.1 Kcal/mole from an approximate  $^1\text{H}$  NMR method<sup>7)</sup> and  $\Delta G^\ddagger$  to be 10.5 Kcal/mole (at  $-41.0^\circ\text{C}$ ) from the coalescence temperature method.<sup>8)</sup>  $\Delta G^\ddagger$  obtained in this work is almost coincident to the latter value when they are compared at the same temperature.  $E_a$  of 4 is considerably smaller than those of 1 and 2 ( $E_a$ 's for 1 and 2 are  $12.7$ <sup>3)</sup> and  $14.5$ <sup>4)</sup> Kcal/mole, respectively), while it is much larger than that of 3 (5.1 Kcal/mole).<sup>6)</sup>

We wish to thank Mr. K.Nakazono for his assistance in the synthesis of barbaralone and the measurement of  $^{13}\text{C}$  NMR spectra.

#### Literatures and Notes

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- 9) Barbaralone was prepared from cyclooctatetraene.<sup>10)</sup>  $^{13}\text{C}$  NMR spectra were recorded on a NEVA NV-14 FT spectrometer (15.087MHz). The concentration of the sample was 15 Wt% in a  $\text{CS}_2\text{-CD}_2\text{Cl}_2\text{-CD}_3\text{COCD}_3$  (14:3:1) solvent system. The sample was completely degassed.  $T_1$ 's were determined by the usual  $180^\circ\text{-}\tau\text{-}90^\circ$  pulse sequence method. The temperature was read by a calibrated copper-constantan thermocouple. The complete line shape analyses were performed using the EXNMRO computer program<sup>11)</sup> with the modified Bloch equation method.
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(Received February 28, 1975)