Tetrahedron Letters No. 20, pp 1803 - 1806, 1974. Pergamon Press. Printed in Great Britain.

NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS. V.[1]

A STUDY ON THE COPE REARRANGEMENT OF BULLVALENE BY ^{13}C NMR

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(Received in Japan 2 March 1974; received in UK for publication 8 April 1974)

3,4-Homotropylidene and its bridge derivatives (e.g.bullvalene(1)) make a Cope rearrangement in a thermal process.[2,3] Recently much attention has been focused on these compounds from dynamic NMR spectroscopy[4,5] as well as synthetic and photochemical standpoints.[6,7] Moreover, in a theoretical field, the activation energies of the Cope rearrangement in these compounds have also been calculated using various molecular orbital methods.[8,9]

Since the ^{1}H NMR spectra of these compounds show complicated line shapes because of various spin couplings between many protons included, it is very difficult to make a line shape analysis for the spectra using accepted methods (e.g. density matrix method), although the activation energy of 1,for example, was able to be determined approximately.[10,11] On the other hand, the proton decoupled ^{13}C NMR spectra of these compounds show simplified spectral patterns, so that the complete line shape analysis of the spectra can be easily accomplished by means of modified Bloch equations to obtain accurate activation parameters of the rearrangement. Along this line, we have recently determined the kinetic parameters for this process of a cyclooctatetraene dimer A (2).[4]

In this paper, we present the results of the complete line shape analysis of the temperature-dependent ^{13}C NMR spectra of bullvalene and report its Cope rearrangement activation parameters.

^{13}C NMR spectra were recorded on a NEVA NV-14 spectrometer operating at 15.1 MHz with a Varian NV-14 computer system for an FT mode. The concentration of the sample was ca. 10 Wt% in deuteriochloroform. The temperature was read by a calibrated copper-constantan thermocouple.

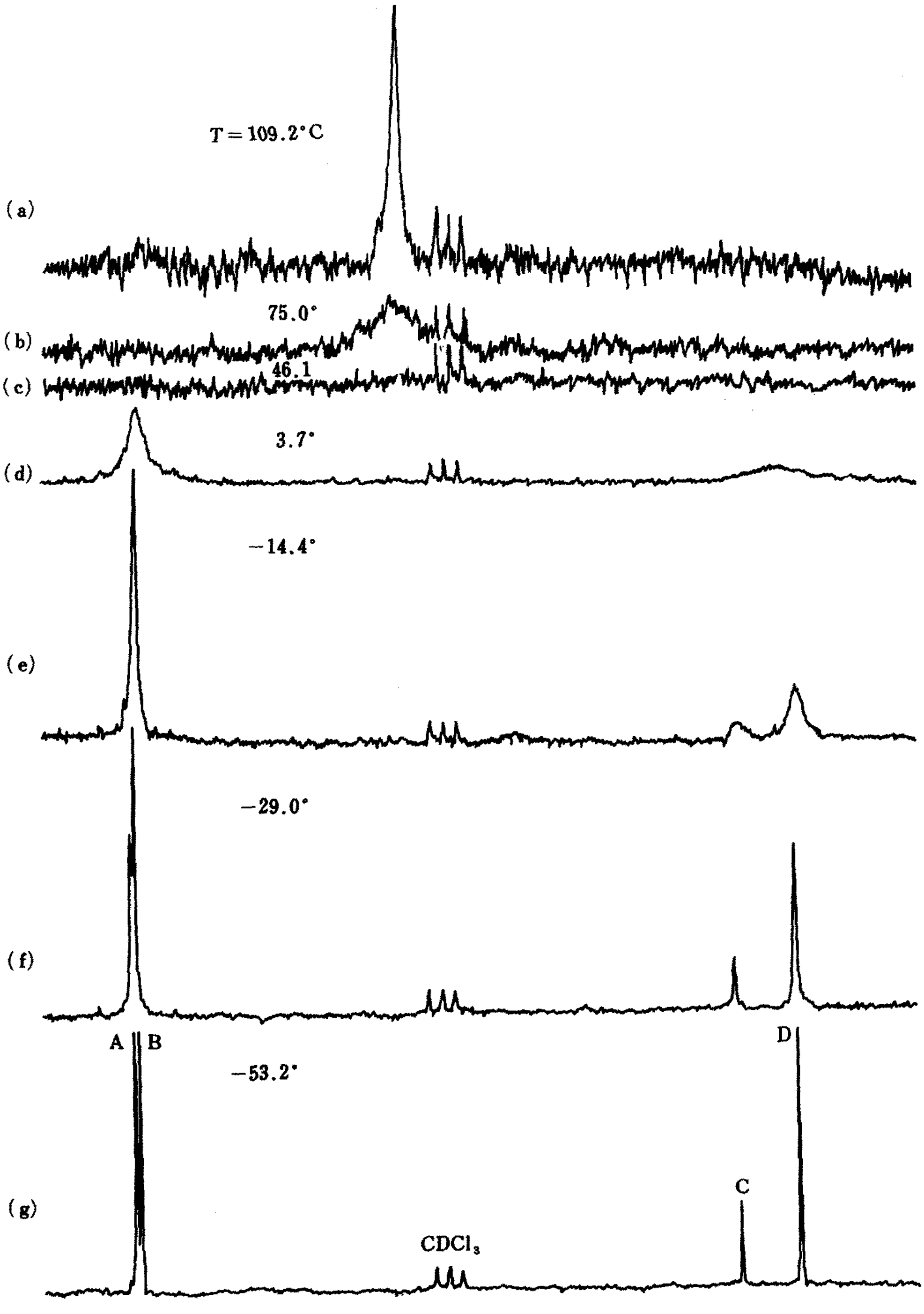
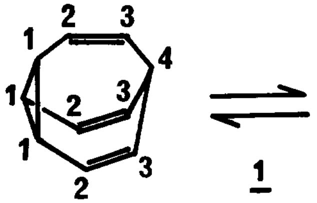


Fig.1. ^{13}C NMR spectra of 1 at several temperatures in $CDCl_3$.

Fig.2. One exchange pass of Cope rearrangement of 1.



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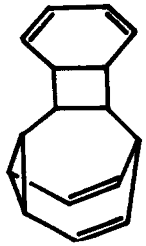

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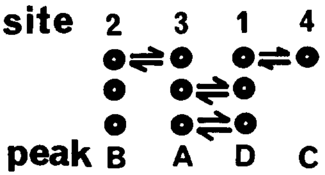
The temperature-dependent ^{13}C spectra of 1 are shown in Fig. 1. At -53.2°C, the spectrum consists of four singlet peaks at 130.0, 129.3, 32.2, and 22.6 ppm down-field from TMS. At temperatures below -53.2°C, the line shape remains almost unchanged. This means that the rate of Cope rearrangement of 1 is sufficiently low at the temperatures on the NMR time scale. As the temperature is raised, all peaks begin to broaden: each of the two pairs of the peaks A,B and C,D coalesces into one broad signal,respectively. At temperatures above 24°C, the two coalesced broad peaks again begin to collapse into one broad signal. From 35°C to about 55°C, the signal is hidden in the noise. At about 60°C, a broad signal appears at the average field of the four chemical shifts at the low temperature, and then the signal becomes sharper as the temperature is increased. This means that the Cope rearrangement of 1 occurs rapidly at about 100°C, and the carbons at all sites exchange with each other.

As shown in Fig.2, the rearrangement of 1 is an exchange between the four sites. The number of the carbons at sites (1),(2),(3), and (4) is 3,3,3, and 1, respectively. Judging from its intensity, the peak C in the spectrum at -53.2°C (Fig.1(g)) can be immediately assigned to the carbon at site (4). Since it is well known that a chemical shift of a three-membered carbon is at a higher field than that of a double bond carbon, the peak D is assigned to carbons at site (1). Then peaks A and B should be assigned to the double bond carbons. It is obvious from Fig.2 that the rearrangement of 1 is constructed from the following exchange scheme: Only one carbon of the three at site (2) exchange with one carbon at site (3), while the other two carbons at site (3) exchange with two carbons at site (1). This indicates that the signal for the site (3) must begin to broaden at a lower temperature than that



for the site (2) carbons. This can be seen from the spectrum at -29.0°C (Fig.1). Thus the lowest field peak A can be assigned to carbons at site (3), and the peak B to carbons at site (2). The chemical shift tendency found in 1 that the peak for a double bond carbon adjacent to a three-membered ring is at a higher field than that of another double bond carbon is in accordance with the result found in a structurally analogous compound 2.[4]

With the above assignment, the complete line shape analysis of the ^{13}C NMR spectra of 1 was performed at 35 temperatures by means of a computer program EXNMRO[12] using modified Bloch equations. The lifetimes of the rearrangement were determined by fitting the calculated spectra with the observed ones at each temperature. The Arrhenius plot between log k and 1/T shows a good straight line from -38.9°C to 109.2°C. The activation parameters obtained are as follows:

$$\begin{array}{llll} Ea = 14.5 \pm 0.7\ \text{Kcal/mole} & \Delta G^{\ddagger} = 12.6 \pm 0.1\ \text{Kcal/mole} & & \\ & & & \text{at } 25.0^{\circ}\text{C} \\ \Delta H^{\ddagger} = 13.9 \pm 0.7\ \text{Kcal/mole} & \Delta S^{\ddagger} = 4.4 \pm 2.3\ \text{e.u.} & & \end{array}$$

The activation energy obtained in this work is larger than the previously reported approximate values (11.8 and 12.8 Kcal/mole from ^{1}H NMR[10] and spin-echo NMR method[11], respectively). It is worthwhile pointing out that the activation energy of 1 is considerably larger than that of 2 (12.7 Kcal/mole).[4]

The authors express their hearty thanks to Mr. T.Muraki for his assistance in the synthesis of bullvalene and the measurement of ^{13}C NMR spectra.

References

1) Part IV: H.Nakanishi and O.Yamamoto,Tetrahedron in press. 2) G.Schröder,J.F.M. Oth, and R.Merenyi, Angew.Chem.,77,774 (1965). 3) G.Schröder and J.F.M.Oth,ibid., 79, 458 (1967). 4) H.Nakanishi and O.Yamamoto, Chem.Lett., 1973, 1273. 5) L.G. Greifenstein, J.B.Lambert, M.J.Broadenhurst,and L.A.Paquette, J.Org.Chem.,38,1210 (1973). 6) A.G.Anaslassiou,A.E.Winston,and R.Reichmanis, J.Chem.Soc.,Chem.Commun. 1973,779 and references therein. 7) H.Tsuruta, T.Kumagai, and T.Mukai, Chem.Lett. 1973, 933 and its references. 8) H.Iwamura, K.Morio, and T.L.Kunii, Bull.Chem. Soc.Japan, 45,841 (1972). 9)M.J.S.Dewar and W.W.Scheller, J.Amer.Chem.Soc., 93, 1481 (1971). 10) M.Saunder, Tetrahedron Lett.,1963, 1699. 11) A.Allerhand and H. S.Gutowsky, J.Amer.Chem.Soc., 87,4092 (1966). 12) O.Yamamoto, K.Hayamizu, H. Nakanishi, and M.Yanagisawa, J.Nat.Chem.Lab.Ind.(Tokyo), 69, 14 (1974).