J. MUSHER (J. I. MUSHER) and A. A. AKHREM

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structural formulas I–VIII

Figure 1: structural formulas I–VIII

Abstract

Full Text

J. MUSHER (J. I. MUSHER) and A. A. AKHREM

STUDY OF THE CONFIGURATION OF SATURATED CYCLIC SYSTEMS BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

2-METHYL-1-OXYCYCLOHEXYLETHYLENE OXIDES AND SOME 1-OXYDECALYLETHYLENE OXIDES

(Presented by Academician B. A. Kazanskii, 21 VI 1960)

One of us, together with Nazarov and co-workers (1−4), on the basis of chemical experiment and concepts of conformational analysis, established the configuration of a series of derivatives of cyclohexane and decalin. Somewhat later, the configuration of cyclohexane derivatives was confirmed (5) by spectra of combinational light scattering. At that time

were also found the preferred conformations of these compounds, which are in an equilibrium mixture with their rotational isomers, and a generalization was made concerning the stereochemistry of nucleophilic addition to the carbonyl group of 2-substituted cyclohexanones and cis- and trans-decalones-1 (6). It was of great interest to investigate the configuration of the compounds obtained by the method of nuclear magnetic resonance (hereafter—NMR), which has high resolving power. In the present article the NMR spectra of four cyclohexane derivatives (I—IV) and four decalin derivatives (V—VIII) are studied. The spectra were obtained by one of us (7) in the physics laboratory of Harvard University in the USA. In all the compounds investigated, one of the substituents is ethylene oxide. The investigation was carried out on a Varian NMR spectrometer at Harvard University at a fixed frequency of 40 MHz, and partly on the equipment of the Mellon Institute at a fixed frequency of 60 MHz. The substances were studied in solution, in carbon tetrachloride; hexamethyldisiloxane was adopted as the internal standard. Chemical shifts and frequency splittings were determined with an accuracy of up to 0.3-0.7 Hz.

The principal region of investigation in the present work is the hydrogen atoms of the ethylene oxide ring; they are all different in their position: one of the two hydrogen atoms at the β-carbon atom of the oxide ring is in the cis-, and the

Fig. 1

Figure 2: Fig. 1

other in the trans-position with respect to the hydrogen atom at the α-carbon atom of the oxide ring. These three atoms may be regarded as a system of three closely interacting spins.

Let us denote, in accordance with (^{8}), by A, B, C nonequivalent nuclei of one and the same kind, whose chemical shifts are of the same order of magnitude as the interaction of their spins. By X, Y, Z⋯we shall denote another series of nuclei, the signals of which are not so close to the signals of A, B, C⋯The nuclei of the series X, Y, Z⋯may or may not be of the same kind as A, B, C ⋯What is essential for us here is that the chemical shift between the groups A, B, C⋯and X, Y, Z⋯is large in comparison with the spin interaction. With such notation, interactions in a system of three spins may be represented in the form A_3, AB_2, AX_2, ABX, etc. Usually, even a visual analysis of the spectrum of such a system makes it possible to determine approximately to which type of the indicated interactions the system under study belongs. Thus, in our case (see Fig. 1 and Table I), compounds I, V, VII, VIII and one of the conformations of compound II (see below) are characterized by interactions of the AB_2 type.

Fig. 1

Further, according to (^{9}), for a three-spin system of the type of the hydrogen atoms of the ethylene oxide ring it was found that, if it is not fused to the cyclohexane ring or is oriented axially to it, then the spectrum proves to be of the ABX type, with an octet for the AB frequencies and a quartet or an overlapping quartet for the X frequencies. If, however, the ethylene oxide ring is oriented equatorially to the ring, then a characteristic AB_2 spectrum is obtained (an octet with one or another splitting of the frequencies; see Fig. 1 and Table 1).

Thus, in compounds I, V, VII, VIII and one of the conformations of II (see below) the ethylene oxide ring is arranged axially, while in compounds III, IV, VI and one of the conformations of II (see below) this ring is arranged equatorially. In the case of an ABX spectrum, the frequencies of the X-hydrogen atom bonded to the α-carbon atom of the ethylene oxide ring are located on the side of smaller field values; A is the hydrogen atom with the larger coupling constant, is in the cis-position with respect to the X-hydrogen atom, and its frequencies are located on the side of larger field values (^{9}). In the case of an AB_2 spectrum, apparently, the frequencies of the A-hydrogen atom are located on the side of smaller field values relative to the frequencies of the B-hydrogen atoms; the A-hydrogen atom is (judging by the large values of the spin-spin coupling constants in most cases) one of the β-hydrogen atoms, namely that situated in the cis-position with respect to the hydro-

to the hydrogen at the α-carbon atom; the other two hydrogen atoms, being in the trans position, are identical magnetically, and their frequencies lie on the side of higher field values. The mutual position of hydrogen atoms A, B, X in the ABX system and of atoms A, B, B in the AB_2 system, as applied to the hydrogen atoms of the ethylene oxide ring, is denoted in accordance with the foregoing by means of A, B, X placed next to the H symbol of the hydrogen atoms of the ring in the scheme of compound II given at the beginning

Table 1

Observed peaks of the protons of the ethylene oxide ring at 40 MHz

Compound	δ_3*	AB	AB	AB	AB	AB	AB	AB	AB	X	X	X
Compound	δ_3*	8	7	6	5	4	3	2	1	12	11 and 10	9
I	97.2	0	3.65	5.83	9.82	9.82	13.88	16.82	19.80	19.80	23.30	27.17
II **	100.0											
V	101.3	0	3.69	6.17	10.0	10.0	13.42	16.30	19.43	21.48	24.92	28.15
VII	97.4	0	3.62	5.37	8.37	8.37	11.21	13.90	16.95	30.0	33.5	36.9
VIII	97.2	0	3.92	5.87	10.17	10.17	13.59	16.59	19.89	30.8	34.3	37.94

Compound	δ_3*	8	7	6	5	4	3	2	1
II **	110.0								
III	111.1	–	−10.86	−6.74	−6.74	−4.34	0	5.2	–
IV	113.2	−13.7	−9.35	−9.35	−9.35	−3.60	0	3.5	–
V	112.0	–	−9.25	−6.45	−5.35	−3.40	0	4.75	–

* Chemical shifts of the 8 and 3 peaks (in Hz) at 40 MHz, referred to hexamethyldisiloxane with a positive sign toward the low-field side.

** Chemical shifts for II were determined at 60 MHz and multiplied by the correction factor $^2/_3$.

Table 2

Calculated parameters for the ethylene oxide ring (Hz)

Compound	Conformation*	J_{AB} 60 MHz	J_{AB} 40 MHz	J_{AX} 60 MHz	J_{AX} 40 MHz	J_{BX} 60 MHz	J_{BX} 40 MHz	$\delta = \nu_B - \nu_A$ 60 MHz	$\delta = \nu_B - \nu_A$ 40 MHz	$\delta = \nu_A - \nu_X$ 60 MHz	$\delta = \nu_A - \nu_X$ 40 MHz	$\frac{J_{AB}}{\delta_{AB}}$
I	a	–	6.0	–	4.2	–	3.1	–	8.7	–	18.0	–
II	e	4.4	–	–	–	–	–	−14	–	–	–	0.4
II	a	5.3	–	2.8	–	2.8	–	11.3	–	21.6	–	–
III	e	6.2	7.5	–	–	–	–	−10.3	−8.3	–	–	0.6
IV	e	–	6.8	–	–	–	–	–	−11.3	–	–	0.4
V	a	5.6	6.2	3.6	3.7	2.8	3.0	11.4	7.6	26.6	18.9	–
VI	e	5.4	6.5	–	–	–	–	−9	−7.1	–	–	0.6
VII	a	5.5	5.5	3.7	4.0	2.8	2.9	8.9	5.8	44.2	28.2	–
VIII	a	5.5	6.1	4.1	2.3	2.5	2.9	10.7	8.1	37.7	28.7	–

* Position of the ethylene oxide ring in the molecule.

of the article. The chemical shifts and spin-spin coupling constants were obtained approximately, using the corresponding schemes and tables for AB_2 and ABX in [8], and are given in Table 2. There the axial (a) and equatorial (e) position of the ethylene oxide ring in the conformation is also indicated. In the NMR spectrum of compound II, more than 12 theoretically possible principal peaks are observed for the system of hydrogen atoms of the ethylene oxide ring of the ABX type. At the same time, in the NMR spectrum of the methyl group of compound II, four peaks (two doublets) are observed instead of the two peaks (one doublet) that should be expected if only one type of methyl group were present in this compound. These circumstances, and the directions of the chemical reaction in obtaining compound II, compel one to assume,

that compound II exists in an equilibrium mixture of two conformations: as a conformation with an axial position of the ethylene oxide ring, characterized by an ABX-type spectrum with 12 peaks, and as a conformation with an equatorial position of the ethylene oxide ring, characterized by an AB_2-type spectrum with 8 peaks.

In the NMR spectrum of compound I, 12 frequencies of the hydrogen atoms of the ethylene oxide ring were observed, characteristic of an ABX system with an axial position of the oxide ring. Proceeding from general considerations, it may be assumed that this configuration differs from the configuration of compound II, also with an axial oxide ring, by a different position of the latter; namely, in I the oxygen atom of the ring is arranged so that it interacts with the equatorial hydroxyl (hydrogen bond). This isomer is the most stable; it is characterized by a higher melting point than compound II, in the predominant conformation of which the ring is also axial. Table 2 gives the values of the ratio $I_{AB}/(\delta = (\nu_B - \nu_A))$ for conformations with an equatorial position of the ethylene oxide ring at a frequency of 60 Mc. For compounds II and IV it is equal to 0.4; for compound III, 0.6. The identical value of this ratio for one of the conformations of compound II and for compound IV is apparently due to the same position of the ethylene oxide ring in these compounds, different from the position of the latter in isomer III with a higher melting point (see the scheme at the beginning of the article).

As is known, the NMR spectra of cis- and trans-decalins differ sharply: the cis isomer is characterized by one sharp peak, the trans isomer by a two-peak broad band (8). On the basis of the study of the NMR spectra we believe that decalols V and VI belong to the trans-decalin series, and decalols VII and VIII to the cis-decalin series. In decalol VI the NMR spectrum belongs to the AB_2 type (see Fig. 1 and Table 1), and, consequently (see above), its ethylene oxide ring occupies an equatorial position. In decalol V the NMR spectrum belongs to the ABX type (see Fig. 1 and Table 1); consequently (see above), its ethylene oxide ring is axial. From this follows the necessity of reversing the configurations of compounds V and VI, which had previously been assigned to them on the basis of incomplete chemical data (4). In decalol VI the ratio $I_{AB}/(\delta = (\nu_B - \nu_A))$ (see Table 2) is the same as in compound III. On this basis we suppose that the position of the ethylene oxide ring in configuration VI is the same as in III. With respect to the mutual position of H_9 and the ethylene oxide ring, compound VI is cis-ae, compound V is trans-aa. Decalols VII and VIII have ABX-type NMR spectra (see Fig. 1 and Table 1), and, consequently, their ethylene oxide rings are axial. The difference between VII and VIII is apparently due to erythro-threo isomerism of the oxide ring.

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Physical Laboratory Harvard University, USA N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.