Soviet-era science, translated into English

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Chemistry

1963

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Fig. 1. P.m.r. spectra of α-3,4-epoxycarane (a) and β-3,4-epoxycarane at $\nu_0 = 24.458$ MHz (b). At right are shown two possible configurations of the half-chair for the conformer α-3,4-epoxycarane. Chemical shifts were determined with an accuracy of 0.04 p.p.m.

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Abstract

Full Text

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PROTON N.M.R. SPECTRA AND THE CONFORMATION OF Δ^3-CARENE OXIDE

Chemistry

In work [1] we proposed conformational formulas for the oxides of α- and β-pinenes, Δ^3-carene and its oxide.

For Δ^3-carene oxide, on the basis of the nonequivalence of two methyl radicals of the gem-dimethyl group, conformation A^* was proposed (Fig. 1). If this nonequivalence is due to the unequal diamagnetic influence of the oxide ring on the protons of the methyls of the gem-dimethyl grouping, then, as we pointed out, for the stereoisomeric form B the nonequivalence of the protons of the gem-dimethyl radicals should not be observed in the p.m.r. spectrum.

Fig. 1. P.m.r. spectra of α-3,4-epoxycarane *(a)* and β-3,4-epoxycarane at $\nu_0 = 24.458$ MHz *(b)*. At right are shown two possible configurations of the half-chair for the conformer α-3,4-epoxycarane. Chemical shifts were determined with an accuracy of 0.04 p.p.m.

In a recent paper by Kuchinskii and Khabudzinskii (2), the synthesis of the second stereoisomer of Δ^3-carene oxide was described, named β-3,4-epoxycarane, in contrast to the α-isomer—the product of epoxidation of Δ^3-carene.

In the present work a comparative study of the p.m.r. spectra of both isomers was carried out. β-3,4-Epoxycarane was synthesized by the method of Kuchinskii and Khabudzinskii (2) and had the constants: b.p. 67°/10 mm, $n_D^{20} = 1.4679$, $\alpha_D = -1.35°$. The constants of α-3,4-epoxycarane were as follows: b.p. 74°/12 mm, $n_D^{20} = 1.4652$, $d^{20} = 0.9525$, $\alpha_D = +14.5°$. The spectra were recorded by a self-recording high-resolution n.m.r. spectrograph YaMR-KGU-1 at $\nu_0 = 24.458$ MHz with a relative resolution of $5 \cdot 10^{-8}$ (3), achieved without

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Fig. 2. NMR spectra of Δ^3-carene. The upper spectrum was recorded at $v_0 = 40$ MHz on a JNM spectrometer of "Japan Electron Optics Laboratory Co" ; the lower, at $v_0 = 24.458$ MHz on a YaMR-KGU-1 spectrometer

Figure 2: Fig. 2. NMR spectra of Δ^3-carene. The upper spectrum was recorded at $v_0 = 40$ MHz on a JNM spectrometer of "Japan Electron Optics Laboratory Co" ; the lower, at $v_0 = 24.458$ MHz on a YaMR-KGU-1 spectrometer

electrical shimming of the magnet. A super-stabilizer of the magnetic flux was used. The sawtooth scanning voltage was supplied from an NGPK-3 generator to coils located on the n.m.r. signal probe. The sweep rate of the magnetic field was 0.7 oersted/sec. Chemical shifts were determined on the Tiers scale (4) and expressed in millionths of the applied field (p.p.m.) with an accuracy of ±0.04 p.p.m. or ±1 Hz.

The integral intensities of the lines were obtained by rounding the relative peak areas to the nearest integer and are indicated everywhere in parentheses.

As is seen from Fig. 1*a*, in the NMR spectrum of α-3,4-epoxycarane, in the region of stronger magnetic fields, three narrow peaks of equal intensity are observed. The first of these peaks, with $\tau = 8.90$ ppm (3), arose from resonance of the protons of the methyl group adjacent to carbon C_4 of the oxide ring. Indeed, in (5) there is an indication of the value of the chemical shift of a methyl radical at an oxide ring, equal to $\tau = 8.88$ ppm, which agrees well with the value given above.

Thus, the methyl peak at the oxide ring is shifted to the paramagnetic side. Here the magnitude of the chemical shift was affected by the electronegativity of the oxygen atom. But if the epoxide ring were magnetically isotropic, then the chemical shift of the methyl CH_3 at atom C_7 would be considerably smaller, as, for example, in the case of tert-butyl alcohol ($\tau = 8.69$ ppm). The higher shift value, equal to $\tau = 8.90$ ppm, indicates the action of the magnetic anisotropy of the epoxide ring. According to Waugh (6), we may assume that in the epoxide ring the distribution of the density of electrons involved in molecular orbitals is almost the same as in the case of a cyclopropane ring. At the center of the ring, owing to overlap of the hybrid sp^2 carbon atomic orbitals whose axes lie in the plane of the ring, there is an increased probability of finding electrons.

Fig. 2. NMR spectra of Δ^3-carene. The upper spectrum was recorded at $v_0 = 40$ MHz on a JNM spectrometer of "Japan Electron Optics Laboratory Co" ; the lower, at $v_0 = 24.458$ MHz on a YaMR-KGU-1 spectrometer.

It must be supposed that in the vicinity of the axis of symmetry located perpendicular to the plane of the ring, a diamagnetic effect on the nuclear magnetic

* If the cyclohexane ring of Δ^3-carene oxide is taken to have the half-chair form, as in cyclohexene oxide, then carbon C_1 is located above the plane C_2, C_3, C_4, C_5, and C_6 below the plane.

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shielding may arise. Indeed, in the case of α-3,4-epoxycarane, the hydrogens of one of the methyl groups of the gem-dimethyl grouping fall under the diamagnetic influence of the oxide ring; therefore their chemical shift is anomalously large and is equal to $\tau = 9.35$ ppm. The hydrogens of the second methyl group experience this influence to a lesser extent, and their shift is equal to $\tau = 9.15$ ppm.

Four cyclohexane protons give rise to absorption bands with $\tau = 8.40$ ppm (case *a*) and $\tau = 8.22$ ppm (case *b*). The great width of these bands indicates that both protons at the same carbon atom have different chemical shifts. At first glance it is not apparent to which line the protons of the CH groups of the cyclopropane ring contribute. Measurement of the integral intensities of the peaks shows that in case (*a*) their peak coincides with the methyl peak at $\tau = 9.35$ ppm, while in case (*b*) they give a peak with $\tau = 9.60$ ppm. Such an interpretation is also confirmed by analysis of the NMR spectrum of Δ^3-carene shown in Fig. 2. Here the methyl

the peak with $\tau = 9.07$ ppm would have an intensity equal to 5 instead of 3, if two cyclopropane hydrogens did not contribute to it. The high value of the chemical shift of these hydrogens is explained by the fact that, owing to sp^2 hybridization of the atomic orbitals of the cyclopropane carbons, the valence angle H—C—H is larger than tetrahedral and amounts to $116°15'$ (7). Therefore the cyclopropane hydrogens experience a fairly strong diamagnetic influence of the three-membered ring. The relative integral intensities of the peaks of α-3,4-epoxycarane, equal, according to the theory, to the number of protons contributing to a given line, are in the ratio $(1:4:3:3:5)$, which confirms the above interpretation of the NMR spectrum.

In the NMR spectrum of β-3,4-epoxycarane (Fig. 1b), the diamagnetic influence of the epoxide ring on the methyl radicals of the gem-dimethyl grouping is not manifested. Therefore both methyls are chemically equivalent, and their protons resonate at one and the same field value, corresponding to a chemical shift $\tau = 9.20$ ppm, close to the chemical shift of the gem-dimethyl group that has not undergone a shift under the influence of the oxide ring. In other respects the spectrum is analogous to the NMR spectrum of the first conformer.

In the spectra of both oxides of Δ^3-carene the peaks at $\tau = 7.47$ ppm and $\tau = 7.50$ ppm have a triplet structure. This multiplicity is due to indirect spin-spin coupling of the moment of the proton at C_3 with the moment of the protons at C_2, with a constant $J = 3$ Hz.

From the spectra presented it is evident that the chemical shifts of the protons in the two isomers differ somewhat from one another. This difference may be caused by the magnetic anisotropy of the C_4—C_7 ordinary bond. As shown in works (8-10), along the C—C bond there appears a region of paramagnetic shift bounded by the surface of a cone with an angle of $55°44'$. In work (11) it was shown that in the cyclohexane ring of epoxycyclohexane the carbon atoms $C_2C_3C_4C_5$ lie in one plane, while atoms C_1 and C_6 leave the

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plane, as shown for α-3,4-epoxycarane on the right in Fig. 1b, c. If in the case of the 3,4-epoxycaranes the same configuration is also retained, then, as is readily seen from simple geometrical models, the van der Waals interaction between the hydrogens of the methyl radical of the gem-dimethyl grouping and the hydrogens either at carbon C_2 (case b) or at carbon C_5 (case c) should lead to a planar arrangement of the carbon atoms $C_2C_1C_6C_5$. If such an effect actually occurs, then the cyclohexane ring will have the conformation of a half-chair, and one of the methyl radicals of the gem-dimethyl grouping may be rather strongly subjected to the influence of the diamagnetic anisotropy of the epoxide ring. Consequently, from the shift of the "chemical shift" of the protons of the gem-dimethyl grouping, one may, using McConnell' s theory (12), study the configuration of the electron density of the epoxide ring.

The NMR spectral data thus confirm the proposition of the diamagnetic influence of the epoxide ring, similar to the diamagnetic influence of the C=C bond, and thereby support the conformational structures for the oxides of bicyclic terpenes proposed by us earlier (1).

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named after A. M. Butlerov
at Kazan State University
named after V. I. Ulyanov-Lenin

Received
March 4, 1963

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