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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF BICYCLIC TERPENES AND THEIR OXIDES BY THE METHOD OF PROTON MAGNETIC RESONANCE

For bicyclic terpenes there are only scattered data in the literature on their p.m.r. spectra. Such are the data on the p.m.r. of camphor, α-chloro-, α-bromo- and $\alpha\alpha'$-dibromocamphor (^{1}), and camphene (^{2}). There are indications of the frequencies of certain p.m.r. lines of α- and β-pinenes (^{3}), and of pinocamphone (^{3}). We have found no data on the p.m.r. spectra of oxides of bicyclic terpenes.

In the present work the p.m.r. spectra of $d\Delta^3$-carene, the oxide of $d\Delta^3$-carene, $d\alpha$-pinene, l-α-pinene, $dl\alpha$-pinene, d-oxide of α-pinene, l-oxide of α-pinene, β-pinene, oxide of β-pinene, semicyclic carenol, and dl-trans-pinocarveol have been studied.

The spectra were recorded on a nuclear magnetic resonance spectrometer with a permanent magnet at $\nu = 24.458$ Mc/s ($H_0 = 5730$ oersted). The spectrograph was developed by Yu. Yu. Samitov; the limiting relative resolving power was $5 \cdot 10^{-8}$. Benzene was used as an internal standard; the diameter of the cylindrical ampoules was 3.0 mm with a sample volume of about 0.1 cm^3. The positions of the lines were determined by the "side-band" method with an accuracy of ± 1 cps and were checked by interpolation between two standards with a relative accuracy of $\pm 0.4 \cdot 10^{-7}$. The spectra were photographed directly from the screen of an ENO-1 oscillograph, with the curvature of the screen taken into account; the field sweep rate was 0.5 oe/sec.

Fig. 1

Figure 1 gives the spectrum of $d\alpha$-pinene. The spectra of $l\alpha$-pinene and dl-α-pinene proved, as was to be expected, identical with the spectrum of $d\alpha$-pinene. The spectrum contains five peaks with the following values of the chemical shifts, referred to benzene, in units of 10^{-7} (ten-millionths of the applied field): 22.1 (1); 50.6 (4); 55.2 (5); 58.8 (3), and 63.3 (3). In parentheses are indicated the approximate relative integral intensities of the peaks, whose numerical values should, according to theory, correspond to the number of protons in the molecule contributing to the given line. The chemical shift 22.1 should be assigned to

Fig. 2

Figure 2: Fig. 2

the proton at the double bond; this value agrees with the literature data for the proton at $C = C$. In Conroy' s review (4) there is an indication of the value of the chemical shift of the methyl radical at the double bond of α-pinene, equal to $\tau = 8.37$, which agrees well with the value 55.2 obtained by us (we assumed that the position of the benzene peak on the τ scale is determined by the value 2.84 (4)). The chemical shifts 58.8 and 63.3 correspond to two methyl radicals of the gem-dimethyl grouping. The high value of the shift for one of the methyl radicals (63.3) and the large difference between the shifts of the two methyl groups (4.5 units) are noteworthy. This phenomenon will be discussed later. It is somewhat more difficult, at the present resolution of the spectrum, to identify the chemical shifts for the methylene groups and the protons of the pinane bridge. In our opinion, the line with the value 50.6 is due to

on the protons of the methylene group next to the double bond and the protons of the pinane bridge, while the protons of the other methylene group contribute to the line with chemical shift 55.2. Figure 1 gives the spectrum of l-oxide of α-pinene (the spectra of d-oxide of α-pinene and of α-pinene are identical to the spectrum of l-oxide) with the following chemical-shift values: 43.6 (1); 53.8 (6); 59.3 (6); 63.8 (3).

Fig. 2

Comparison of the spectrum of pinene oxide with that of α-pinene indicates the disappearance of the line with shift equal to 22.1, corresponding to the proton at C=C, and the appearance of a peak with value 43.6, corresponding to the proton at the oxide ring (for –CH–C with O in the ring, in furmagiline the values given are $\tau = 7.20 \div 7.65$, or, relative to benzene, 43.6-48.1 (2)). It should be noted that in the spectrum of α-pinene oxide the chemical shift for the methyl at the oxide ring is 59.3, i.e., close to the value 60.6 reported for the methyl radical at the oxide ring in furmagiline (2), and that the two peaks with high chemical-shift values for the gem-dimethyl groups are retained, and the shift of the methyl group at the oxide ring is increased.

Figure 2a presents the PMR spectrum of β-pinene. Four main peaks are observed in the spectrum, with values 25.3 (2); 49.3 (8); (57.8 (3); 62.6 (3). It is evident from the spectrum that the peak 49.4 is poorly resolved. In it a peak with chemical-shift value 54.6 (2) is indicated. The shift 25.3 may be assigned to the protons of the methylene group of the semicyclic bond (for camphene values of 24.0 and 27.5 are given (2)). The lines with shifts 62.9 and 57.9 are due to the gem-dimethyl group. The spectrum of β-pinene, recorded on a spectrograph with greater resolving power (Japan Nuclear Magnetic Resonance Spectrometer), confirmed the assumption concerning the complexity of the peak with value 49.3, as is evident from the spectrum presented in Fig. 2b. We have

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

not assigned the chemical shifts in the interval 44–54 to definite protons of the β-pinene molecule.

Fig. 3

The spectrum of β-pinene oxide is presented in Fig. 2c. The values of the chemical shifts and their intensities are characterized by the following data: 47.1 (2);

53.1 (8); 59.6 (3) and 63.2 (3), and a poorly resolved peak is also outlined in the region of 50 (1). The spectrum of β-pinene oxide is close to the spectrum of α-pinene oxide, with the exception of the lines from the protons at the oxide ring. In β-pinene oxide these protons give lines with higher shift values, which corresponds to the literature data on the chemical shift of the grouping CH_2-O-C (for isobutylene oxide the value of the chemical shift is 46 (^{2})). The chemical shifts 63.2 and 59.6 should be assigned to the methyl radicals of the gem-dimethyl grouping. The poorly resolved peak corresponds to the six protons of the methylene groups and to the two protons of the pinane bridge.

Fig. 4

In Fig. 3 is presented the spectrum of $d\Delta^3$-carene with five peaks: 20.0 (1); 51.8 (4); 55.1 (5); 60.3 (3); 62.3 (3). The resonance at 20.0 is due to the proton at the double bond. The position of the peak from the protons of the methyl group at the double bond, equal to 55.1, is close in value to that of the analogous methyl group in α-pinene (55.2). The peaks 62.3 and 60.3 correspond to the gem-dimethyl radicals. The methylene groups, evidently, should be represented by the values 51.8. It was not entirely clear to which line the CH groups of the cyclopropane ring contribute. In a preliminary communication on the structure of cycloheptatriene derivatives, Corey, Burke, and Remers (^{7}) give the NMR spectrum of Δ^2 4-methylcaren-5-one, in which the protons of the cyclopropane ring are assigned to the line with value 54.8. Therefore, in the case of Δ^3-carene the protons of the cyclopropane ring may be assigned to the peak with value 55.1, to which the protons of the $CH_3—C=$ group also contribute.

The NMR spectrum of $d\Delta^3$-carene oxide is presented in Fig. 3. The following values of chemical shifts were obtained: 47.1 (1); 55.9 (6); 60.5 (3); 62.4 (3) and 65.4 (3). In the spectrum there is no peak with value 20.0, which corresponded to the proton at the double bond, but a peak with value 47.1 appears, corresponding to the proton at the oxide ring. The values 65.4 and 62.4 correspond to the gem-dimethyl groups, the line 60.5 to the methyl radical at the oxide

Chemical structures: (I) α-pinene, (II) β-pinene, (III) Δ^3-carene; conformations of α-pinene oxide, β-pinene oxide, and Δ^3-carene oxide showing "interaction" and "no interaction" ; (IV) trans-pinocarveol.

Figure 5: Chemical structures: (I) α-pinene, (II) β-pinene, (III) Δ^3-carene; conformations of α-pinene oxide, β-pinene oxide, and Δ^3-carene oxide showing "interaction" and "no interaction" ; (IV) trans-pinocarveol.

ring, and the peak 55.9 is due to the methylene groups and the protons of the cyclopropane ring. The data from the NMR spectra of bicyclic terpenes and their oxides show that the presence of an epoxide ring is excellently proved by the NMR method ([3]).

Analysis of the NMR spectra of bicyclic terpenes and their oxides also makes it possible to draw certain conclusions about their conformation. The high shift values of the methyl groups of the gem-dimethyl groupings of bicyclic terpenes and the different shift values of each of these methyl groups indicate the presence of a diamagnetic shift undergone by one of the gem-dimethyl groups. The reason for this is the magnetic anisotropy of the double bond. A group falling within the conical region above or below the plane of the double bond experiences a diamagnetic shift (the line is shifted toward larger field values). Thus, in the case of α- and β-pinenes, only one of the gem-dimethyl groups experiences a diamagnetic shift (of the order of 2-3 ten-millionths of the applied field ([3])). Such a displacement is in good agreement with the conformation of α- and β-pinenes ([9]) (see formulas I and II). As for Δ^3-carene, there are no exact data on its conformation. The considerable difference in the chemical shifts of the gem-dimethyl groups (2 units) indicates the presence of diamagnetic shielding by the double bond of one of them also in the case of $d\Delta^3$-carene (see formula III).

Comparison of the NMR spectra of the oxides of bicyclic terpenes with the spectra of the initial bicyclic hydrocarbons shows that in the case of oxi-

these chemical shifts, corresponding to the geminal methyl groups, have high values and retain different shift values for each of the geminal methyl groups (63.8 and 59.3 for α-pinene oxide, 63.2 and 59.6 for β-pinene oxide, and 65.4 and 62.4 for Δ^3-carene oxide). Thus, in the case of the oxides as well there are diamagnetic shifts for one of the geminal methyl groups. Evidently, the diamagnetic shift in this case is due to the oxide ring and may indicate the conformation of the oxides of bicyclic terpenes.

We also studied the p.m.r. spectra of two alcohols of the bicyclic series. The spectrum of trans-pinocarveol is shown in Fig. 4; it has the following chemical-shift values: 23.1 (1); 25.5 (1); 29.5 (1); 36.4 (1); 51.7; 60.3 (3) and 66.2 (3). The values 23.1 and 25.5 evidently belong to the methylene group of the semicyclic bond; the shift 29.5, to the proton of the hydroxyl group, as shown by the addition of methyl alcohol to the sample. The shift 36.4 belongs to the proton on the carbon to which the hydroxyl group is attached. The latter follows from comparison with literature data for analogous groupings[9]. The peak 51.7 receives contributions from the protons of the methylene groups and the protons of the pinane bridge. The absorption lines with values 60.3 and 66.2 correspond to the methyl protons of the gem-dimethyl grouping. In this case too, one of the methyl groups has a diamagnetic shift (see formula IV). The spectrum of semicyclic carenol consists of broadened lines, and therefore it was not completely analyzed.

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