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CHEMISTRY

1965

SovietRxiv

Abstract

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UDC 541.634

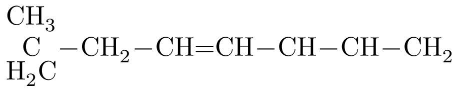
CHEMISTRY

Academician B. A. ARBUZOV, A. R. VIL' CHINSKAYA,
Yu. Yu. SAMITOV, L. K. YULDASHEVA

ON THE STRUCTURE OF ALLOOCIMENE DIOXIDE

The aliphatic terpene alloocimene is readily oxidized by atmospheric oxygen to a honey-like polymeric peroxide, which spontaneously converts into a monomeric dioxide ([1], [2]).

Desalbre, Laurcad, and Rapp ([3]) assigned to the dioxide structures I, Ia, or II. Subsequently, Nave, Desalbre, and Ardizio ([4]), on the basis of a study of the products of reduction of the dioxide, came to the conclusion that the dioxide has structure (II).



$$\overset{CH_3}{\underset{H_2C}{C}}-CH_2-CH{=}CH-CH-CH-CH_2 \qquad (I)$$

$$(CH_3)_2C-CH-CH{=}CH-CH-CH-CH_2 \qquad (Ia)$$

$$(CH_3)_2C-CH-CH{=}CH-C(CH_3)-CH-CH_3 \qquad (II)$$

Taking into account the presence in the IR spectrum of the dioxide of a frequency of 970 cm^{-1}, the authors come to the conclusion that the double bond near C_4–C_5 is in the trans position. Since the initial alloocimene, according to ([5]), represents a mixture of trans- and cis-C_6–C_7 forms, Nave, Desalbre, and Ardizio believe that the dioxide may represent a mixture of trans- and cis-C_6–C_7 compounds. Dranishnikov ([6]) holds a different opinion concerning the structure of alloocimene dioxide. On the basis of the oxidation of the tetritol obtained by hydration of the dioxide and its dihydro derivative, Dranishnikov arrives at dioxide structure III

$$(CH_3)_2C-CH-CH-CH-C(CH_3){=}CH-CH_3 \qquad (III)$$

Since the conclusions on the structures of dioxides II and III are based on products of reduction or hydration of the dioxide, in which isomerization processes

Fig. 1. NMR spectrum of alloocimene dioxide

Figure 1: Fig. 1. NMR spectrum of alloocimene dioxide

are possible, we used the proton magnetic resonance (p.m.r.) spectrum to establish the structure of the dioxide. The dioxide was synthesized according to the directions of Dranishnikov (^{2}) and had the following constants: b.p. 89-89.5°/7 mm, n_D^{20} 1.4632, d_4^{20} 0.9534. Thin-layer chromatography on alumina gave one spot, indicating the homogeneity of the oxide. The p.m.r. spectrum of the dioxide, recorded on a YaMR-2303 spectrometer at a frequency of 60 MHz, is presented in Fig. 1.

The spectrum contains a complex band with shift $\delta = 5.61$ ppm, corresponding to 2H and belonging to the protons at the double bond. This band arose from the superposition of the doublet $C_4(H)$, produced by spin interaction with $C_3(H)$, and the peak $C_5(H)$. The multiplet with $\delta = 3.11$ ppm corresponds to the hydrogen at $C_3(H)$. The spin quartet at $\delta = 2.80$ ppm with $J_{HH} = 6.2$ Hz is due to resonance of one hydrogen at the other oxide ring $[C_7(H)]$. A band of sharp peaks ($\delta = 1.16,\ 1.25$, and 1.29 ppm), corre-

···accounting for 12H, belongs to the methyl radicals at the oxirane ring. The peak at $\delta = 1.29$ ppm may be assigned to the protons of CH_3 at C_6; the line with $\delta = 1.25$ ppm receives a contribution from the protons of the methyl $C_1(H_3)$, while the methyl geminal to it resonates at $\delta = 1.16$ ppm. The protons of the methyl $C_8(H_3)$ give a doublet merging with the peaks of the latter band ($\delta = 1.25$ and 1.16 ppm).

Fig. 1. NMR spectrum of alloocimene dioxide at $\nu_0 = 60$ MHz (NMR spectrometer RYa-2303) at 23°C. Tetramethylsilane (TMS) was added as an internal standard, $\delta_{\text{TMS}} = 0$.

From the spectrum in Fig. 1 and from the assignment given above it is evident that the chemical shifts of the protons of the oxirane rings $C_3(H)$ and $C_7(H)$ do not coincide, and that the shift of methyl $C_6(H_3)$ differs from the shifts of the other terminal methyls. This fact is due to the circumstance that the proton $C_3(H)$ is located in the nodal plane of the π-bond of the group $> C = C <$, while the protons $C_6(H_3)$ rotate near this plane. Consequently, the resonance of these protons must be displaced somewhat toward lower fields. Indeed, estimating the displacement by the McConnell formula (^{7}),

$$\Delta\sigma^{\text{AH}} = \frac{1}{3NR^3}\sum_i (1 - 3\cos^2\gamma_i)\chi_{ii},$$

assuming $\chi_{zz} > \chi_{xx} \approx \chi_{yy}$ and $\Delta\chi_{\text{C=C}} = -6.2 \cdot 10^{-6}$ cm^3 mol^{-1}, we obtain $\Delta\sigma_1[C_3(H)] = 0.24$ ppm and $\Delta\sigma_2[C_6(H_3)] = 0.12_6$ ppm.* The somewhat underestimated value of $\Delta\sigma_1$ in comparison with the experimental one is explained by violation of the dipole approximation. Thus, these estimates support the assignment made and, consequently, the choice of structure II.

In the case of structure III, the spectrum of the dioxide should have contained a peak of the proton at the double bond with integral intensity 1H and an intense peak in the region of 1.80 ppm from two $CH_3{-}C$ groups (see, for example, the NMR spectrum (^{8}) of alloocimene), which are absent from the spectrum.

Since the UV spectra of the dioxide indicate a trans arrangement of the groups at $C_4{-}C_6$, as in the starting alloocimene,** its dioxide should be

(IV) (V)

to assign structure IV or V. These structures differ in the mutual arrangement of the oxide rings. In IV the vectors of the dipole moments of the oxide rings are directed to the same side, in V to opposite sides. Determination of the dipole moment of the dioxide in benzene solution gave $\mu = 4.05\,D$, which corresponds approximately to the sum of two dipole moments of ethylene oxide. For structure V one could expect a dipole moment close to zero. Thus, alloocimene dioxide should be assigned structure IV.

It is believed that alloocimene consists of 64-65% of the C_4-trans-C_6-cis isomer and 35-38% of neoalloocimene (the C_4-trans-C_6-trans isomer (^{8})); therefore for alloocimene dioxide isomer IV would also seem possible, but with a trans arrangement of the methyl groups at the C_6—C_7 oxide ring. This question requires further clarification.

Finally, it should be noted that instead of the expected sharp doublet of the proton at C_3, which should have arisen as a result of spin interaction with the adjacent proton at the double bond, the NMR spectrum shows a complex multiplet band ($\delta = 3.11$ m.u.). In addition, on the right side of the methyl-proton band there is a small peak. These features of the NMR spectrum can be explained by the presence in the dioxide, as an impurity, of a stereoisomeric dioxide. After completion of the present work, we became aware of a study by Doyle and co-workers (^{10}), in which alloocimene dioxide was investigated by NMR and IR spectroscopy. By careful fractionation of a large amount (4 l) of the dioxide, the American authors succeeded in isolating, in amounts of 5% each, two stereoisomeric dioxides. To one of them Doyle and co-workers assign structure II with the trans-C_4—C_5 configuration, and to the other—structure II with the cis-C_4—C_5 configuration. Doyle does not consider the spatial arrangement of the oxide rings.

* The averaging was carried out over 6 positions of the methyl protons. The value $\Delta\chi_{C=C} = -6.2 \cdot 10^{-6}$ cm^3 mol^{-1} was obtained by us from analysis of the NMR spectra of α- and β-pinene.

** Alder, Drayke, Erpenbach, and Wicker (^{9}) regard alloocimene as the C_{4-5} trans-C_{6-7} trans form and neoalloocimene as the C_{4-5} trans-C_{6-7} cis form.

Comparison of the NMR spectrum of alloocimene dioxide obtained by us with the NMR spectra reported by Doyle for trans-C_4—C_5 dioxide and cis-C_4—C_5 dioxide permits the conclusion that the sample of dioxide studied by us consists mainly of trans-C_4—C_5 dioxide and contains a relatively small amount of the isomer to which Doyle assigns the structure of cis-C_4—C_5 dioxide.

Scientific Research Chemical Institute
named after A. M. Butlerov
at Kazan State University

Received
17 IV 1965

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