AN INVESTIGATION IN THE FIELD OF THE STEREOCHEMISTRY OF ACETYLENIC α-OXIDES

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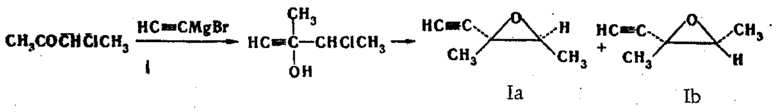
In the synthesis of 3-methyl-2,3-epoxypent-4-yne by the action of powdered caustic potash on 4-chloro-3-methylpent-1-yn-3-ol, a mixture of cis and trans oxides is formed with predominance of the isomer to which, on the basis of the PMR spectroscopy of saturated and acetylenic α-oxides, the cis configuration of the methyl groups has been ascribed.

Acetylenic α- oxides are usually obtained by the action of solid caustic potash and the corresponding chlorohydrins which, in their turn, are synthesized from Iotsich reagents and α-chloro carbonyl compounds. The latter reaction is nonstereospecific and, in the general case, may lead to the formation of diastereomers. The subsequent closure of the oxide ring should give a mixture of cis-and trans-isomeric oxides.

The present paper describes the synthesis of 3-methyl-2,3-epoxypent-4-yne (I) by the following route:



The α- oxide (I) is formed in quantitative yield and, according to GLC and to PMR spectroscopy, it forms a mixture of cis- and trans-isomers (Ia and Ib) in a ratio of 4:1. The predominant isomer was isolated by fractionation through a column, and in its PMR spectrum (Table 1) the signal of the proton attached to the oxide ring was in a weaker field and the signals of the protons of the methyl groups and of the proton on the acetylenic bond were in a stronger field than the corresponding signals in the spectrum of the second isomer.

For comparison, the PMR spectra of the oxides (II-VII) were taken (see Table 1). In the PMR spectra of the unsymmetrical disubstituted saturated oxides (II) and (III), the protons attached to the oxide ring give a single broad signal with δ 2.37 ppm. In the spectrum of the monosubstituted oxide (IV), the signals of the protons at the β-carbon atom have δ 2.28 and 2.54 ppm. Comparison with the spectra of the oxides (II) and (III) permits an assignment of the signal at 2.54 ppm to the proton present in the trans position and that at 2.37 ppm to the proton in the cis position relative to the alkyl group. Thus, the alkyl group screens the proton on the neighboring carbon atom of the oxide ring, which is in the cis position, in harmony with literature information [1-3]. In the spectrum of the oxide (V), the signals of the protons on the β-carbon atom of the oxide ring have fairly close chemical shifts, i.e., the acetylenic grouping exhibits similar effects on the protons in the cis and trans positions. In the spectra of the acetylenic oxides (VI) and (VII), one of the protons gives a signal at the same values of δ as the protons of the oxide (V). The signal of the other proton is shifted upfield. By comparing the spectra of compounds (II-VII) it is possible to conclude that in the acetylenic α- oxides (VI and (VII), the relative positions of the signals of the protons attached to the oxide ring are determined mainly by the locations of these protons relative to the alkyl grouping on the α-carbon atom of the oxide ring, and therefore the signal of the proton in the cis position is present in the region of higher fields.

Thus, the predominating isomer of the oxide (I), characterized by the appearance of the signal of the proton attached to the oxide ring at lower field strengths, has the cis configuration (Ia). This is also

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TABLE 1. PMR Spectra of the α Oxides

Compound	R*	δ, ppm	R′	δ, ppm	R″	δ, ppm	R‴	δ, ppm
Ia	HC≡C	2,15	CH_3	1,36	H	3,05	CH_3	1,20
Ib	HC≡C	2,25	CH_3	1,40	CH_3	1,30	H	2,77
II	P-C_3H_7	1,41	CH_3	1,17	H	2,37	H	2,37
III	P-C_6H_{13}	1,41	CH_3	1,17	H	2,37	H	2,37
IV	P-C_3H_7	1,42	H	2,73	H	2,28	H	2,54
V	CH_3C≡C	1,76	H	3,12	H	2,68	H	2,64
VI	HC≡C	2,15	CH_3	1,46	H	2,83	H	2,56
VII	CH_3C≡C	1,74	CH_3	1,39	H	2,73	H	2,52

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*In the alkyl radicals, the values of δ for the CH_2 group closest to the oxide ring are given.

confirmed by the positions of the signals of the methyl groups. In the spectrum of the predominating isomer they are at higher field strengths. A similar phenomenon has been observed in the spectra of the cis and trans but-2-enes, where the signals of the methyl groups of the cis isomer are also present in the region of higher fields [4].

A comparison of the PMR spectra of the saturated (II-IV) and the acetylenic (V-VII) oxides shows that the replacement of an alkyl group by an acetylenic group leads to a downfield shift of the signals of the protons attached to the β-carbon atom by 0.2-0.3 ppm and to the α-carbon atom by 0.4 ppm.

The IR spectra of the oxides (Ia, V-VII) and of the mixture of the oxides (Ia and Ib) are extremely similar in the 1200-1300 cm^{-1} and 800-900 cm^{-1} regions which are characteristic for the vibrations of an oxide ring [5]. The spectra of the pure oxide (Ia) and of the mixture of oxides (Ia) and (Ib) are very similar. In this case, IR spectroscopy does not provide the possibility of judging the presence of isomeric compounds and is therefore unsuitable for determining their configurations.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in the 700-3600 cm^{-1} region (the pure substances were used at a layer thickness of 18 μ). The PMR spectra were taken on a Varian HA-100-D/15 instrument with HMDS as internal standard using 10% solutions in carbon tetrachloride. Gas-chromatographic analysis was performed on a Tsvet-1 chromatograph with a flame-ionization detector using a column 2m × 0.4 cm. The stationary phase was dinonyl phthalate (10%) on Celite-545. The rate of flow of the carrier gas (H_2) was varied according to the structure of the substances being investigated. For purification, the oxides were redistilled through a column with glass packing (15 theoretical plates).

3-Methyl-2,3-epoxypent-4-yne (I). The ethylmagnesium bromide obtained from 24 g (1 g-atom) of magnesium and 109 g (1 mole) of ethyl bromide in 500 ml of tetrahydrofuran was added in small portions in a current of acetylene with cooling to a saturated solution of acetylene in tetrahydrofuran. After the end of the addition, acetylene was passed through the reaction mixture for another 5 h and then, with cooling, a solution of 95 g (0.88 mole) of 3-chlorobutan-2-ol in tetrahydrofuran was added. The resulting complex was decomposed with 5% hydrochloric acid, and the organic layer was salted out and was dried with magnesium sulfate. Distillation yielded 106.9 g of 4-chloro-3-methylpent-1-yn-3-ol, bp 72.5-73.5°C (60 mm); 157-158°C (760 mm); d_4^{20} 1.0690; n_D^{20} 1.4615. With stirring, 120 g (2.1 mole) of powdered KOH was added to an ethereal solution of 107 g (0.75 mole) of the chlorohydrin. The ethereal layer was dried with magnesium sulfate, and the ether was evaporated off. The residue was evaporated, first at 100 mm, bp 58-59°C, and then at atmospheric pressure. This gave 74 g (96%) of 3-methyl-2,3-epoxypent-4-yne (I), bp 108-110°C; d_4^{20} 0.8838; n_D^{20} 1.4255. Found %: C 74.9; H 8.5. C_6H_8O. Calculated %: C 75.0; H 8.4.

The cis isomer (Ia) was isolated by fractionation through a column, bp 109.5-110°C; d_4^{20} 0.8855; n_D^{20} 1.4273. Found %: C 74.9; H 8.4. C_6H_8O. Calculated %: C 75.0; H 8.4. IR spectrum, cm^{-1}: 760 s, 860 s, 920 w, 940 w, 985 s, 1040 m, 1080 s, 1120 m, 1150 s, 1235 s, 1310 m, 1390 s, 1420 m, 1450 m, 1460 s, 2125 w, 2890 w, 2940 s, 2980 s, 3010 s, 3300 s.

The oxides (II-VII) were synthesized in a similar manner to (I) [in the case of compounds (II-V and VII) absolute ether was used as the solvent]. The constants of the chromatographically pure saturated and acetylenic oxides have been given previously [6].

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