Chemistry

Academician of the Academy of Sciences of the Kazakh SSR M. I. Goryaev and G. A. Tolstikov

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Fig. 1

Figure 1: Fig. 1

reaction scheme

Figure 2: reaction scheme

Abstract

Full Text

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The Structure of Sabinene Monohydrochloride

Semmler (^1), who first studied the hydrochlorination reaction of sabinene, obtained the monohydrochloride in about 30% yield and assigned to it the structure of 1-chlorothujane (I). Wallach (^2) succeeded in somewhat increasing the yield of sabinene monohydrochloride, for which he proposed the structure 1-methylene-4-chloro-4-isopropylcyclohexane (II). It is characteristic that in the modern literature

Fig. 1

on terpene chemistry this contradiction has remained. Thus, in Grignard' s *Treatise of Organic Chemistry* (^3), structure II is given for sabinene monohydrochloride, whereas Simonsen (^4) prefers to use Semmler' s formula I. We have been able to establish that carrying out the hydrochlorination reaction of sabinene at −30–40° makes it possible to obtain an almost quantitative yield of the monohydrochloride. As to the structure of this sabinene derivative, neither Semmler' s formula nor Wallach' s formula appears to us correct.

Fig. 2

The principal argument against structure II is the presence of optical activity in sabinene monochloride. For an unambiguous determination of the structure of sabinene monohydrochloride we recorded the infrared spectra of sabinene and terpinenol-4. The IR spectrum of the monohydrochloride

sabinene (see Fig. 1) contains a band of weak intensity at about 1674 cm^{-1},

Fig. 2

Figure 3: Fig. 2

Reaction scheme: sabinene is protonated to a menthyl cation, followed by chloride addition to give 4-chloro-menthene-1 (III).

Figure 4: Reaction scheme: sabinene is protonated to a menthyl cation, followed by chloride addition to give 4-chloro-menthene-1 (III).

Fig. 3. IR spectrum of sabinene.

Figure 5: Fig. 3. IR spectrum of sabinene.

characteristic of a double bond. A similar frequency was also found in the IR spectrum of terpineol-4 (Fig. 2), whereas sabinene (Fig. 3) has a high-intensity absorption band at about 1652 cm^{-1}.

Both the spectrum of sabinene monohydrochloride and the spectrum of terpineol contain the frequencies 810 and 3020 cm^{-1}, which are characteristic of a trisubstituted double bond. Sabinene absorbs at about 890 and 3075 cm^{-1} (methylene group) and at about 1028 and 3045 cm^{-1} (cyclopropane ring).

Thus, sabinene monohydrochloride should be assigned the structure of 4-chloro-menthene-1 (III), the formation of which may be represented by the following scheme:

Experimental Part

13.6 g of sabinene ($n_D^{20}1.4677$; $d_4^{20}0.8441$; $[\alpha]_D^{20}+102.5°$), previously distilled in a stream of dry argon over metallic sodium, was dissolved in 75 ml of dry petroleum ether, and the solution was saturated with a stream of thoroughly dried hydrogen chloride. The temperature of the reaction mixture was maintained at about −30, −40°. After the usual workup, the product was distilled in vacuo. This gave 16.4 g (95%) of sabinene monohydrochloride, having: b.p. 71-74°/1 mm, $n_D^{20}1.4837$; $d_4^{20}0.9850$; $[\alpha]_D^{20}7.1°$. $C_{11}H_{17}Cl$. MR calculated 50.55; found 50.12.

Fig. 3

Institute of Chemical Sciences
Academy of Sciences of the Kazakh SSR

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