Chemistry

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

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Figure 1: reaction scheme: cedrol (II) gives α-cedrene (I) plus β-cedrene (III)

reaction scheme 1: cedrenal (IV) converted through intermediates (V), (VI), (VII), (VIII) to cedrenes

Figure 2: reaction scheme 1: cedrenal (IV) converted through intermediates (V), (VI), (VII), (VIII) to cedrenes

Abstract

Full Text

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Synthesis of β-Cedrene

Natural cedrene, in comparison with α-cedrene I, obtained by dehydration of cedrol II, has a smaller angle of rotation. Nav, Papazyan, and Leprotte ([1]) showed that this difference is explained by the inhomogeneity of the natural product.

Identification of the products of oxidative cleavage of substituted cyclopropanecarboxylic acids, synthesized by the authors named above by condensation of natural cedrene with ethyl diazoacetate, allowed them to conclude that the natural hydrocarbon contains an admixture of β-cedrene III —a compound with an exocyclic double bond.

The formation of natural cedrene must proceed according to the following scheme:

However, β-cedrene has so far not been obtained in the individual state. In the present work the synthesis of β-cedrene is described.

The course of the synthesis, based on the reaction described by Treibs ([2]) for oxidation of cedrene with selenium dioxide to cedrenal IV, may be represented by Scheme 1.

Scheme 1

It proved impossible to obtain β-cedrene by dehydrobromination of primary cedranyl bromide, since the latter was not changed by the action of alcoholic alkali, boiling ethylpyridine, or sodium ethylate. Pyrolysis of primary cedranol 3,5-dinitrobenzoate VI led to the formation of a mixture of α- and β-cedrenes.

Fig. 1. IR spectrum of α-cedrene obtained by dehydration of cedrol. NaCl, LiF prisms, $l = 4\mu$, IKS-14

Figure 3: Fig. 1. IR spectrum of α-cedrene obtained by dehydration of cedrol. NaCl, LiF prisms, $l = 4\mu$, IKS-14

The IR spectrum of the pyrolysis product, along with the frequencies 1625, 3075, and 887 cm^{-1}, characteristic of

the group $R_2C{=}CH_2$, contains frequencies 1660 and 3022 cm^{-1}, characteristic of the secondary-tertiary double bond of α-cedrene. Apparently, the severe reaction conditions (280-350°) cause isomerization of β-cedrene into α-cedrene. It should be noted that the conversion of β-pinene into α-pinene proceeds so smoothly that this reaction was used by Rudakov to obtain α-pinene of the highest optical purity (^{3}).

We succeeded in obtaining a very pure sample of β-cedrene by pyrolysis of the N-oxide of dimethyl-prim.-cedranylamine VII.

Fig. 1. IR spectrum of α-cedrene obtained by dehydration of cedrol. NaCl, LiF prisms, $l = 4\mu$, IKS-14

According to Cope (^{4}), cleavage of N-oxides of tertiary amines is the mildest method for the pyrolytic preparation of olefins. The β-cedrene obtained by the indicated route is a colorless liquid with the following constants: n_D^{20} 1.5047; d_4^{20} 0.9350; $[\alpha]_D^{20}$ +11.3° (heptane, $C = 13.6$).

The infrared spectrum of β-cedrene contains intense bands at about 1625 and 887 cm^{-1} and a band with frequency 3075 cm^{-1}, which are characteristic of an exomethylene double bond. Hydrogenation on platinum gives cedrane, very close in properties to cedrane from α-cedrene.

Experimental Part

α-**Cedrene** was obtained by dehydration of cedrol isolated from the essential oil of Cossack juniper (*Juniperus sabina* L.), and had the following constants: n_D^{20} 1.4982; d_4^{20} 0.9343; $[\alpha]_D^{20}$ –93.5°.

Cedrenal was obtained by a somewhat modified Treibs procedure (^{2}) in a yield of 72-75% as against 50-55% indicated by the cited author; n_D^{20} 1.5195; d_4^{20} 1.0202; $[\alpha]_D^{20}$ –65.5°.

Primary cedranol was obtained in quantitative yield by hydrogenation of cedrenal over skeletal nickel at 70 atm and 60°. Colorless viscous liquid: b.p. 143-144/1 mm; n_D^{20} 1.5095; d_4^{20} 1.0110; $[\alpha]_D^{20}$ –17.0°; MR found 65.68, calculated 66.29.

Found, %: C 80.66; H 11.80
$C_{15}H_{26}O$. Calculated, %: C 81.08; H 11.71

Fig. 2. IR spectrum of the product of pyrolytic decomposition of primary cedranol 3,5-dinitrobenzoate. NaCl, LiF prisms, $l = 4\,\mu$, IKS-14

Figure 4: Fig. 2. IR spectrum of the product of pyrolytic decomposition of primary cedranol 3,5-dinitrobenzoate. NaCl, LiF prisms, $l = 4\,\mu$, IKS-14

Fig. 3. IR spectrum of β-cedrene from dimethyl-primary-cedranylamine N-oxide. NaCl, LiF prisms, $l = 5\,\mu$, IKS-14

Figure 5: Fig. 3. IR spectrum of β-cedrene from dimethyl-primary-cedranylamine N-oxide. NaCl, LiF prisms, $l = 5\,\mu$, IKS-14

3,5-Dinitrobenzoate was obtained in the usual manner, m.p. 80.5–81.5° (petroleum ether).

Found, %: N 6.92
Calculated, %: N 6.72

Fig. 2. IR spectrum of the product of pyrolytic decomposition of primary cedranol 3,5-dinitrobenzoate. NaCl, LiF prisms, $l = 4\,\mu$, IKS-14.

Fig. 3. IR spectrum of β-cedrene from the N-oxide of dimethyl-primary-cedranylamine. NaCl, LiF prisms, $l = 5\,\mu$, IKS-14.

Pyrolysis of primary cedranol 3,5-dinitrobenzoate (VI). 7.5 g of (VI) was heated in a heat-resistant flask at 15 mm and 280–350°. The distillate was chromatographed on alkaline aluminum oxide (activity

I–II). Elution with petroleum ether gave 1.30 g (35%) of hydrocarbon: n_D^{20} 1.5055; d_4^{20} 0.9317; $[\alpha]_D^{20}$ −34.6°; *MR* found 65.01, calculated 64.40.

Found, %: C 88.23; H 11.52
$C_{15}H_{24}$. Calculated, %: C 88.17; H 11.83

Dimethyl-prim.-cedranylamine (VIII). 22.2 g of (IV) was hydrogenated over a catalyst of 15 g of Ni/Al alloy in 150 ml of a 4% solution of dimethylamine in ethanol at 120 atm, 80° for 4 h. 8.0 g (32%) of (VIII) was obtained, b.p. 150–152°/1 mm; n_D^{20} 1.5033; d_4^{20} 0.9555; *MR* found 77.21, calculated 78.05. Hydrochloride, m.p. 255.5–256° (acetone).

Found, %: N 4.66
$C_{17}H_{32}NCl$. Calculated, %: N 4.83

In addition, prim.-cedranol was obtained in 60% yield.

Preparation of β-cedrene by pyrolysis of (VII). 5.8 g of amine, 10 ml of acetone, and 7 ml of 28% H_2O_2 were stirred at room temperature until the product had completely dissolved. After decomposition of the excess hydrogen peroxide with platinum black and removal of the solvent in vacuo, the product was pyrolyzed at 150–190°/1 mm. The distillate was washed with hydrochloric acid to remove unreacted dimethyl-prim.-cedranylamine and chromatographed on Al_2O_3 (activity I-II). 1.50 g (31%) of β-cedrene was obtained as a colorless liquid with the following constants: n_D^{20} 1.5047; d_4^{20} 0.9350; $[\alpha]_D^{20}$ +11.3 (heptane, $C = 13.6$); MR found 64.76, calculated 64.40.

Found, %: C 88.08; H 11.72
$C_{15}H_{24}$. Calculated, %: C 88.17; H 11.83

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