BRIEF COMMUNICATIONS

TRANSFORMATIONS OF α -4, 5-EPOXYCARANE UNDER INFLUENCE OF HC1

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Previously it was shown that the reaction of α -3,4-epoxycarane with an other solution of HCl proceeds with opening of the oxide ring at both C-0 bonds [1, 2]. In the present paper we studied the effect of HCl on α -4,5-epoxycarane (I) in order to ascertain the predominant direction of opening the oxide ring when it is found in conjugation with the cyclopropane ring.

It is known that in acid medium both α -2,3-epoxycarane and (I), which have conjugated three-membered rings, form homoallylic rearrangement products that involve the cyclopropane ring [3]. Thus, (I) gives the rearranged (monocyclic) and unrearranged (carane) products in a 2.4:1 ratio. The reaction of (I) with an ether solution of HCl leads to the monocyclic products, namely cis-mementha-4,8(9)-dien-6-ol (IV), cis-mementh-4-en-8-chloro-6-ol (V), and cis-mementh-4-ene-6,8-diol (VI), and the product with a carane structure, namely cis-caran-48-chloro-5 α -ol (II), in a 3.5:1 ratio (based on the weight of the compounds isolated by chromatography in SiO₂) (Scheme 1). In addition, the reaction mixture contained aromatic C₁₀H₁₄ hydrocarbons.

Unsaturated alcohol (IV) and diol (VI) were identified by comparing the constants, as well as the IR and PMR spectral data, with those given in [3]. The unsaturated chlorohydrin of composition $C_{10}H_{17}OCl$ was assigned the monocyclic structure (V) on the basis of the IR and PMR spectral data. The IR spectrum contains bands that are characteristic for a disubstituted double bond. The PMR spectrum contains signals that correspond to two CH_3 groups that are adjacent to a Cl atom [4], two protons of a symmetrically disubstituted double bond, and a multiplet that belongs to a carbinol proton.



A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 10, pp. 2380-2382, October, 1978. Original article submitted August 26, 1977. The carane structure of chlorohydrin (II) follows from the PMR spectral data and conversion to the known cis-caran-5 α -ol [5] by reduction with Na/NH₃. The PMR spectrum has the signals of the protons of the cyclopropane ring and three CH₃ groups, and two triplets that are characteristic for the protons of C atoms that are bonded to C1 and OH atoms.

The formation of the indicated products from (I) under the influence of HCl can be depicted by a scheme where opening of the oxide ring at the C_4 atom gives chlorohydrin (II); opening at the C_5 atom and subsequent homoallylic rearrangement of the intermediate carbonium ion leads to compounds (IV) and (V). Diol (VI) is apparently formed during the competing hydration of the epoxide. The possibility of such a path is indicated by the presence of aromatic hydrocarbons in the reaction mixture, which can be regarded as being dehydration products.

The isomeric carane chlorohydrin (VII), corresponding to cis-caran-5 β -acetoxy-4 α -ol, one of the reaction products of (I) with CH₃COOH [3], was not detected by us.

EXPERIMENTAL

The melting points were determined on a Kofler block. The IR spectra were taken on a UR-10 spectrophotometer. The PMR spectra were recorded on a Varian T-60 instrument using TMS as the internal standard. Silufol plates were used for the TLC. The detection was done by spraying the plates with a 5:90:5 anisaldehyde-ethanol- H_2SO_4 mixture and subsequent heating at 70-80°C.

 α -4,5-Epoxycarane was obtained by the epoxidation of 4-carene with perbenzimidic acid as described in [6]. 4-Carene was synthesized by the pyrolysis of cis-caran-4 α -ol methylxanthate as described in [7]. cis-Caran-4 α -ol was obtained by the hydroboration of 3-carene as described in [5].

Effect of HCl on α -4,5-Epoxycarane (I). The reaction of (I) with HCl was run as described in [1]. We obtained 11.1 g of a solid product from 10 g of (I). A double recrystallization from petroleum ether gave diol (VI) with mp 105-106°; $[\alpha]_D^{20}$ -107.8° (C 5.9, CHCl₃). PMR spectrum (δ , ppm): 1.08 d (3H, 7-CH₃), 1.14 s (6H, 9- and 10-CH₃), 3.7 m (1H, CHOH), 5.8 s (2H, -CH=CH-).

The filtrates from the recrystallization of diol (VI) were chromatographed on SiO_2 to give (II)-(V).

 $\frac{4-\beta-\text{Chloro-cis-caran-}5\alpha-\text{ol} (\text{II})}{1, \text{ bp } 95-96^{\circ} (1 \text{ mm}); n_D^{2\circ} 1.4982; [\alpha]_D^{2\circ} +25.9^{\circ}. \text{ Found:}} C 63.53; H 9.09\%. C_{10}H_{17}OCL. Calculated: C 63.66; H 9.02\%. Infrared spectrum: 1020 cm^{-1} (v_{C-O}). PMR Spectrum (\delta, ppm): 1.09 s (9H, 8-, 9-, 10-CH_3), 3.76 t (1H; CHOH), 4.03 t (1H, CHCl). 3,5-Dinitrobenzoate (3,5-DNB), mp 132-134^{\circ} (MeOH). Found: C 53.35; H 4.98; Cl 9.19\%. C_{17}H_{19}O_6N_2CL. Calculated: C 53.33; H 4.97; Cl 9.28\%. The reduction of 0.37 g of the chlorohydrin with Na (0.25 g) in liquid NH₃ (50 ml) gave 0.2 g of cis-caran-5\alpha-ol (III). 3,5-DNB, mp 115-116° (MeOH).$

 $\frac{\text{cis-m-Mentha-4,8(9)-dien-6-ol} (IV)}{\text{spectrum: 740, 890, 1040, 1645, 3030, 3080 cm^{-1}} (1 \text{ mm}); n_D^{2^{\circ}} 1.4920; \alpha_D - 180^{\circ}. \text{ Infrared spectrum: 740, 890, 1040, 1645, 3030, 3080 cm^{-1}} \text{ PMR spectrum (δ, ppm): 1.08 d (3H, 7-CH_3), 1.69 s (3H, CH_2=CCH_3), 3.67 m (1H, CHOH), 4.7 s (2H, C=CH_2), 5.6 s (2H, CH=CH). 3,5-DNB, mp 145-147^{\circ} (MeOH). Found: N 8.42%. C_{17}H_{18}O_6N_2. Calculated: N 8.09%.$

 $\frac{\text{cis-m-Menth-4-en-8-chloro-6-ol (V), mp 49-50°. Found: C 63.60; H 9.0; Cl 18.71%. C₁₀-H₁₇OCl. Calculated: C 63.66; H 9.02; Cl 18.84%. Infrared spectrum: 740, 1050, 1645, 3030 cm⁻¹. PMR spectrum (<math>\delta$, ppm): 1.07 d (3H, 7-CH₃), 1.5 sand 1.57 s (6H, 9- and 10-CH₃), 3.67 m (1H, CHOH), 5.8 s (2H, CH=CH). 3,5-DNB, mp 139-141° (MeOH). Found: C 53.60; H 5.0; N 7.55%. C₁₇H₁₉O₆N₂Cl. Calculated: C 53.33, H 4.97, N 7.32%.

CONCLUSIONS

The reaction of α -4,5-epoxycarane with HCl proceeds with the preferential opening of the oxide ring at the C₅ atom and the formation of m-menthene derivatives.

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ISOMERIZATION OF 4-CHLOROBUTYL ESTERS OF ALKYLENE GLYCOL PHOSPHORUS ACIDS

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The intramolecular Arbuzov rearrangement of the haloalkyl esters of alkylene glycol phosphorous acids (AGPA) can proceed with either an opening or retention of the glycol ring, depending on the size of the ring, the number of substituents in it, and also on the structure of the haloalkyl group [1-4].

In order to establish the relation between the direction of the Arbuzov reaction in the series of chloroalkyl esters of AGPA and the structure of the chloroalkyl group we studied the isomerization of the 4-chlorobutyl esters of AGPA.



 $R = CH_2CH_2CH_2(I), CH_2CH_2CHCH_3(II), CH_2CHCH_3(III), CH_3CHCHCH_3(IV)$

Cyclic phosphites (I)-(IV) were obtained from the corresponding glycol chlorophosphites and 4-chlorobutyl alcohol in the presence of a base; the constants of phosphites (I)-(III) are given in Table 1. Based on the DTA data, the 4-chlorobutyl esters of AGPA undergo rearrangement at a higher temperature than the corresponding 3-chloropropyl esters, while in the series of the 3-chloropropyl and 4-chlorobutyl esters of AGPA the phosphites with a sixmembered ring are isomerized at a lower temperature than the five-membered phosphites (Table 2). The rearrangement of 4-chlorobutyl esters (I)-(IV) is more complicated than that of the corresponding 3-chloropropyl esters. Together with the intramolecular isomerization products, the yield of which is low (Table 3), compounds that cannot be vacuum-distilled are formed, the treatment of which with PCls leads to 4-chlorobutylphosphonic dichloride (V). This testifies that phosphites (I)-(IV) undergo intermolecular Arbuzov rearrangement. The intramolecular isomerization of phosphites (I)-(III) proceeds predominantly in the first direction, with opening of the alkylene glycol ring independent of its size, to give 1,2-oxaphosphorinane derivatives (A). An exception is (IV), whose isomerization was studied previously. On the basis of analyzing the hydrolysis products of the phosphonate, obtained by the rearrangement of phosphite (IV), it was concluded that its isomerization goes in the second direction to give phosphonate (IV)' (B) [2]. According to our data, the isomerization of phosphite (IV) proceeds predominantly in the second direction to give 2-oxo-2-(4'-chlorobuty1)-4,5-dimethy1-1,3,2-dioxaphospholane with $\delta_{31P} = -48$ ppm. But it is possible via the ³¹P NMR spectrum to also record the formation of a second isomer with a 1,2-oxaphosphorinane ring (A) in an amount of $\sim 20-25\%$, with $\delta_{31P} = -22$ ppm. The ³¹P NMR method was used to establish the structure of the isomerization products of phosphites (I)-(IV). In [3] it was shown that a chemical shift

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