REACTION OF 3,4-DICHLOROCARANES WITH NUCLEOPHILIC REAGENTS

B. A. Arbuzov, Z. G. Isaeva, and G. Sh. Bikbulatova

The 3,4-dichlorocaranes obtained from the chlorination of 3-carene in the presence of $NaHCO_3$ [1] are isomers (I) and (II), respectively with a trans- and a cis-carane structure and a diequatorial and a diaxial orientation of the C-Cl bonds [2]



In order to corroborate the spatial structures assigned to them on the basis of the data of chemical methods, we undertook a study of the reactions of the dichlorides with nucleophilic reagents.

 3α , 4β -Dichlorocarane (I) proved to be more stable under the conditions of the E_2 cleavage reaction (reaction of $t - C_4H_9OK$ in $t - C_4H_9OH$): when heated with the base at 100 °C for 15 h it gives a product that, based on the chlorine content, corresponds to a mixture of dichloride and monochlorides $C_{10}H_{15}Cl$ in a 1:1 ratio. 3β , 4α -Dichlorocarane (II) under the same conditions is converted to a mixture of monochlorides in in 10 h. It proved impossible to identify the monochlorides in view of the complexity of the mixture. Based on the data of the IR spectra, one of the components of the mixture is a monochloride with an unsymmetrically disubstituted double bond, but from the acetolysis products of the monochlorides by chromatographing on silica gel was isolated only a small amount of the acetates of unsaturated alcohols, the IR spectrum of

which also contains bands that are characteristic for the $\sum C = CH_2$ group. By chromatographing the saponi-

fication products of the acetates was isolated an alcohol with a terminal double bond of unknown structure, which forms a 3,5-dinitrobenzoate (3,5-DNB) with mp 119-120°C.

The low reactivity of (I) toward a base caused us to undertake a study of its transformations in S_N^1 nucleophilic substitution reactions. The reaction of (I) with silver acetate in glacial acetic acid gives a complex mixture of products, in which were identified the acetates of 3-caren-7-ol (XIII), p-mentha-1,5-dienn -8-ol (VII), 2-p-tolyl-2-propanol (IX), and 1-methyl-4-isopropenylbicyclo[3.1.0]-2-hexanol (XVI), the diacetate of 3β , 4β -caranediol (XXIII), and 6,6-dimethyl-3-acetylbicyclo[3.1.0]hexane (XXII). In addition, in the acetolysis products was found the acetate of an alcohol of unknown structure, which forms a 3,5-DNB with mp 127-128°C. The isomeric unsaturated acetates were identified mainly by the crystalline esters of the corresponding alcohols. In order to isolate the reaction products we employed chromatographing on silica gel and on aluminum oxide in a column and in a thin layer. The formation of the indicated products from 3α , 4β -dichlorocarane (I) under the influence of silver acetate can be depicted by a scheme, according to which their diversity is explained by the possibility of stabilizing the carbocation that is formed in the heterolysis of the C_4 -Cl bond via the ejection of β -H⁺ in various directions and via the electrophilic attack of the medium

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The nature of the products of the acetolysis reaction is in agreement with its progress via the intermediate chlorides (IV), (XI), (XV), and 4-acetoxy-3-chlorocarane (XIX). As was shown earlier [1], the acetate of 3-carene-7-ol (XIII) is formed as the main product when 3-chloro-4(7)-carene is reacted with AgOAc. The second product of the stabilization of the carbcation along the first direction, namely 3-chloro -4-carene (IV), during substitution undergoes the rearrangement: (V) \rightarrow (VI), which is a type of allyclic rearrangement of 1,3-diene systems, with a shift of the functional group of the δ -position, and gives the acetate of p-mentha-1,5-dien-8-ol (VII) [3-5]. The acetate of 2-p-tolyl-2-propanol (IX) is formed as the dehydrogenation product of (VII) under the reaction conditions. The formation of chloride (XV) is the result of the trans-annular involvement of the cyclopropane ring via a 1,3-shift of the C₆-C₈ bond in the carbocation (III) [6, 7]. The stabilization of carbocation (III) by the addition of acetate ion leads to 3α -chloro- 4β -acetoxycarane (XIX), the acetolysis of which to the diacetate of 3β , 4β -caranediol (XXIII) is accompanied by cleavage reactions, with a rearrangement of the retropinacolin type and the formation of ketone (XXII) [8]. 3β , 4α -Dichlorocarane (II) when reacted with silver acetate in acetic acid also gives a mixture of products, in which we were able to identify only the acetate of 3-caren-7-ol.

EXPERIMENTAL

The melting points were determined on a Kofler block. The IR spectra were taken on a UR-10 instrument; the GLC analysis was run on a Tswett-1 chromatograph, using nitrogen as the carrier gas, Chromsorb W as the solid support, 10% Tween 80 [poly(hydroxyethylenesorbitan monooleate)] as the liquid phase, and a temperature of 140°C.

Action of $t - C_4 H_9 OK$ on $3\alpha, 4\beta$ -dichlorocarane (I). A mixture of 6 g of (I) [mp 34,5-35.5°C, $[\alpha]_D$ 69.4°C (C 4.83, CHCl₃)] and 1.25 g of K in 35 ml of $t - C_4 H_9 OH$ was heated at 95-100°C for 15 h. Then the $t - C_4 H_9 OH$ was distilled off, and the residue was diluted with water and dried over Na₂SO₄. The residue (4.5 g) from the removal of the ether was distilled in vacuo from a small flanged flask; bp 97-99°C (6 mm); α_D 52.6°C; n_D^{20} 1.4987; yield 4.15 g. Found: C 64.62; H 9.03; Cl 26.77%. $C_{10}H_{15}$ Cl. Calculated: C 70.35; II 8.85; Cl 20.78%. $C_{10}H_{16}$ Cl₂. Calculated: C 57.96; H 7.78; Cl 34.26%. Based on the analysis data for the amount of chlorine, only half of the HCl was cleaved from (I). The presence of the starting dichlorocarane (I) and two monochlorides in the mixture was shown by TLC on SiO₂.

Action of $t - C_4 H_9 OK$ on 3β , 4α -dichlorocarane (II). A mixture of 12 g of (II) ($\alpha_D + 101.7^{\circ}C$; n_D^{20} 1.5010) and 2.5 g of K in 65 ml of $t - C_4 H_9 OH$ was heated at 100°C for 10 h. After a workup similar to that described

TABLE 1

| TABLE 1 | | | | TABLE | TABLE 2. | | | | |
|------------------------------|--|-------------------------------|------------------------------|---------------------------------|----------------------|---|--------------------------------|--------------------------------------|--|
| Fr ac- tion No. | bp,°C(p, mm Hg) | Wt., g | ⁿ D ²⁰ | αD | Fraction No. | bp, °C (p, mm Hg) | Wt., g | n_{D}^{20} | α _D |
| I II III IV | $\begin{array}{c} 38 - 40 \ (5) \\ 93 - 103 \ (5) \\ 107 - 123 \ (5) \\ 101 - 112 \ (8 \cdot 10^{-2}) \end{array}$ | $0,62 \\ 6,0 \\ 8,28 \\ 4,31$ | 1,4826 1,4748 1,4748 | +20 +13,4 Not translucent | I II III IV | 42-82 (5) 86-102 (5) 102-105 (5) 103-130 (1) | $1,26 \\ 9,6 \\ 5,49 \\ 23,54$ | 1,4976 1,4840 1,4778 1,4711 | $ \begin{vmatrix} +20,2 \\ +42,3 \\ +47,4 \\ +31,4 \end{vmatrix} $ |

above we obtained 8.2 g of a product with bp 63-69°C (3 mm); $\alpha_D + 34.2$ °C; n_D^{20} 1.4962; d_4^{20} 1.013. Found: C 69.63; H 9.08; Cl 20.36%; MR 49.19. C₁₀H₁₅ClF₁, 3-membered ring. Calculated: C70.35; H 8.85; Cl 20.79%; MR 49.09. Analysis by TLC indicated the presence of two monochlorides in the cleavage products, in the IR spectrum of which were the absorption bands of the C-Cl bond at 620 cm⁻¹, of unsymmetrically disubstituted and trisubstituted double bonds, and also of bands that are characteristic for aromatic compounds $(\nu, \text{ cm}^{-1})$: 825, 890, 1520, 1620, 1655, 1690, 3005, and 3080. The intense absorption band of $\nu_{\rm C-Cl}$ at 620 cm⁻¹ can be assigned to the allylic carenyl chlorides, 3-chloro-4(7)-carene and 3-chloro-4carene, with a cis-position of the C-Cl bond relative to the cyclopropane ring (the IR spectrum of trans-3chloro-4(7)-carane has ν_{C-Cl} 660 cm⁻¹ [1]). The monochlorides reacted to a very slight degree with tetraethylammonium acetate (refluxing in acetone solution for 96 h). A mixture of acetates (1.34 g) was obtained when 4.3 g of the monochlorides was heated with 6.3 g of AgOAc in 30 ml of glacial acetic acid, the IR spectrum of which had absorption bands with the frequencies: 820, 900, 1600, 1640, 1655, 1680, 1730, 3025, and 3070 cm⁻¹. From 0.2 g of the saponification products of the acetates by TLC on SiO₂ we isolated a two-component mixture of alcohols [0.06 g, IR spectrum (ν , cm⁻¹): 890, 1640, 1660, 3075], which formed a 3.5-DNB with mp 119-120°C.

Action of AgOAc on 3α , 4β -Dichlorocarane (I). A mixture of 25 g of (I) and 44.3 g of AgOAc in a mixture of 200 ml of CH₃COOH and 25 ml of (CH₃CO)₂O was heated at 70°C for 55 h. After removal of the precipitate by filtration the acetic acid was distilled off and the residue (28 g) was vacuum distilled from an Arbuzov flask (Table 1). The products of fraction II were chromatographed on SiO2 to give 1.27 g of a mixture of acetates with n_D^{20} 1.4800; α_D + 28°C. The saponification of this mixture (1.2 g) with 2% aqueous alcoholic caustic solution gave 0.87 g of a product with bp 95-105°C (10 mm); n_D^{20} 1.4968; α_D + 42.5°C; the IR spectrum of this product had bands that are characteristic for a terminal double bond ($\nu_{C=C}$ 1645, ν_{C-H} 3070 and 3080, δ_{C-H} 895 cm⁻¹). Based on the TLC data, the saponification product contained a mixture of alcohols, the treatment of which with 3,5-dinitrobenzoyl chloride gave a 3,5-DNB mixture that failed to crystallize. Two 3,5-DNB were isolated when this mixture was chromatographed on SiO₂: 1) mp 94-96°C, which proved to be the 3,5-DNB of p-mentha-1,5-dien-8-ol [9], and 2) mp 126-128°C, not identical with the 3,5-DNB of cis-4(7)-caren-3-ol, which has a close melting point [10].

A mixture of 54 g of dichloride (I) and 95.7 g of AgOAc in 500 ml of glacial acetic acid was heated for 43 h to give 48.8 g of a tarry product, which was separated into four fractions (Table 2) by distillation from an Arbuzov flask. When the products of fractions II-III (see Table 2) were chromatographed on Al₂O₃ (II activity) we obtained 2.6 g of a mixture of acetates with n_D^{20} 1.4754; α_D + 36.2°C. After removal of the dienic acetates from this mixture by treatment with maleic anhydride, the remaining acetates (1.03 g) were saponified with 2% aqueous alcoholic caustic solution. From the saponification product (0.7 g) was obtained 1.3 g of the 3,5-DNB. Chromatographing of the latter gave 0.72 g of a crystalline product with mp 110-124°C, the saponification of which gave 0.24 g of a mixture of alcohols with bp 90-92°C (10 mm); n_D^{20} 1.4910; d_4^{20} 0.9605; IR spectrum (ν , cm⁻¹): 890, 1050, 1070, 1380, 1645, 2730, 3060, and 3080. The oxidation of the alcohols with CrO_3 led to the ketone [IR spectrum (ν , cm⁻¹): 900, 1650, 1690, 1730, 3080]; 2,4-dinitrophenylhydrazone, mp 168-169°C. The mixed melting point with the 2,4-dinitrophenylhydrazone of 1-methyl -4-isopropenylbicyclo [3.1.0]-2-hexanone (XVIII) [7] was not depressed.

The products of fraction IV were fractionally distilled through a column with an efficiency of eight theoretical plates (Table 3). The saponification of 6 g of the acetates from fractions I-III (see Table 3) with 2% aqueous alcoholic caustic solution gave 3.5 g of a product with bp 95-107°C (10 mm), which was separated by chromatographing on Al_2O_3 (Table 4).

The products of fractions I-III (see Table 4) contained 6,6-dimethyl-3-acetylbicyclo[3.1.0]hexane (XXII) (GLC analysis); 2,4-dinitrophenylhydrazone, mp 134-135°C. The mixed melting point with the 2,4dinitrophenylhydrazone of ketone (XXII), synthesized as described in [8], was not depressed.

TABLE 3

| Fraction No. | bp, °C (p · 10 ⁻² , mm Hg) | Wt., g | n_{D}^{20} | αD |
|--|---|---|---|---|
| I III IV VI VII VII IX | 60-62 (3) 62-70 (3) 74-80 (3) 82-86 (3) 87-92 (3) 93-96 (3) 91-92 (2,5) rinæd from column Residue | 2,29 1,59 2,23 2,5 3,42 3,43 2,75 3,42 1,56 | $\begin{array}{c} 1,4782\\ 1,4803\\ 1,4774\\ 1,4778\\ 1,4676\\ 1,4642\\ 1,4634\\ 1,4632\\\end{array}$ | $\begin{array}{c} +54,4\\ +30,4\\ +14,9\\ +23,9\\ +32,7\\ +37,7\\ +39,2\\ +30\\ -\end{array}$ |

TABLE 4

| Eluant | Fraction No. | Volume of eluate, ml | Wt., g | v, cm-1 |
|---------------------------|-----------------|----------------------------|----------------|--------------------------------|
| Petroleum ether (70 - | т | 40 | 0.57 | |
| 100°) | II | 40 | 0,57 | 890, 1650, 3070, 1710 |
| Petroleum ether - diethyl | III IV | 60 40 | 0,14 0,11 | 890, 1650, 3070, 1600, |
| ether (10:1) | v | 60 | 0,181 | 1510 890, 1650, 3070, 1510, |
| | VI VII | 60 60 | 0,12) | 1600 |
| Petroleum ether – diethyl | VIII | 40 | 0,2 | |
| Diethyl ether | X | 40 50 | $0,25 \\ 0,23$ | |
| EthanoI | XI XII | 140 100 | $0,22 \\ 0,85$ | |

Based on the GLC data, fractions VIII-XI contained 3-caren-7-ol (XIV). The treatment of these fractions (0.9 g) with phthalic anhydride (0.54 g) in pyridine gave 0.8 g of the acid phthalate of 3-caren-7-ol with mp 118-120 °C. The part of the product that failed to react with phthalic anhydride weighed 0.45 g; in the IR spectrum were present absorption bands (890, 1520, 1600, 1650, 3080 cm⁻¹) that are characteristic for compounds of the aromatic series and compounds containing a terminal double bond. Based on the GLC data, the product represented a mixture of alcohols, one of which was 1-p-tolyl-2-propanol. However, neither the 3,5-DNB nor the α -naphthylurethan could be obtained.

From the products of the hydrolysis of fractions VI-VIII (see Table 3) with 5% aqueous alcoholic caustic solution was isolated (by extraction with butanol) cis-3,4-caranediol (XXIV) with mp 137°C. The mixed melting point with the 3β ,4 β -caranediol, obtained by the hydration of β -3,4-epoxycarane in acid medium [11], was not depressed.

Action of AgOAc on 3β , 4α -Dichlorocarane (II). A mixture of 3.3 g of (II) and 6 g of AgOAc in 25 ml of CH₃COOH and 10 ml of (CH₃CO)₂O was heated at 75-80°C for 12 h to give 2.1 g of a product with the constants: $\alpha_{\rm D}$ + 29.8°C; $n_{\rm D}^{20}$ 1.4848; d_4^{20} 1.035; the Beilstein test for chlorine was positive. Saponification of 0.93 g of the product with 2% aqueous alcoholic caustic solution gave 0.53 g of a mixture, from which was isolated 0.15 g of alcohols by TLC on SiO₂. Reaction of the alcohols with 3,5-dinitrobenzoyl chloride gave at least two 3,5-DNB (TLC). From the mixture by TLC on SiO₂ was isolated the 3,5-DNB of 3-caren-7-ol (XIV) with mp 77-79°C. Even with repeated TLC on SiO₂, the other 3,5-DNB could not be isolated in a crystalline form.

CONCLUSIONS

 $3\alpha,4\beta$ -Dichlorocarane when subjected to acetolysis undergoes rearrangements that are characteristic for the carane system: " Δ^4 -carene-p-1,5-menthadiene," "caraneethylbicyclohexane," and "caranemethyl-isopropenylbicyclohexane."

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