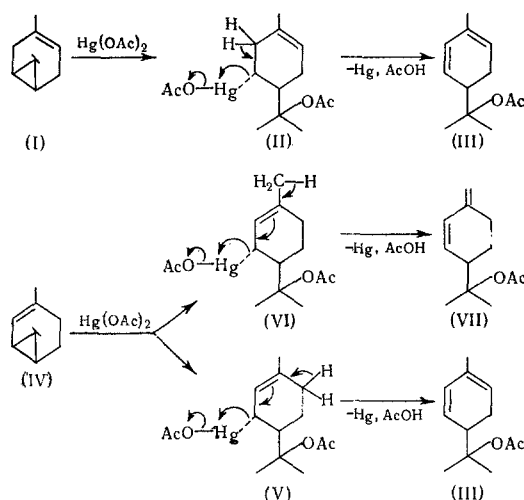


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In a previous paper [1] we had shown that p-menthadienol acetates (III) and (VII) are formed when the 3- and 4-carenes are reacted with $\text{Hg}(\text{OAc})_2$. Their formation was explained via initial attack of the hydrocarbons at the double bond by the oxidizing agent. However, it is known that $\text{Hg}(\text{OAc})_2$ easily adds to a three-membered ring [2-5]. In this case the formation of (III) and (VII) can also be depicted as being the result of adding $\text{Hg}(\text{OAc})_2$ to the 3- and 4-carenes at the cyclopropane ring and the subsequent cleavage of Hg and acetic acid from the corresponding adducts (II) and (VI), which, however, we were unable to isolate.



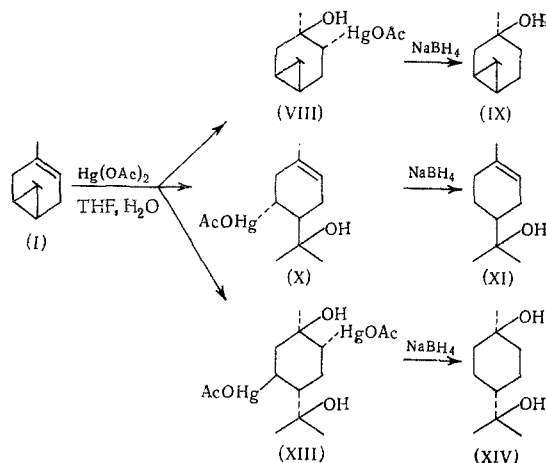
Scheme 1

The purpose of the present study was to ascertain the possibility of adding $\text{Hg}(\text{OAc})_2$ to 3-carene, not only to the double bond, but also to the cyclopropane ring. For this we employed the Brown method [6-8], which consists in the hydroxymercuration of a hydrocarbon with $\text{Hg}(\text{OAc})_2$ in aqueous tetrahydrofuran (THF) and subsequent demercuration by hydrogenolysis with NaBH_4 . During the course of these transformations, 3-carene should give β -4-caranol (IX) in the case of adding the mercury salt to the double bond and either α -terpineol (XI) or m-1-methen-8-ol (XII) if the addition takes place at the cyclopropane ring. Addition in either direction leads to one of the stereoisomeric 1,8-terpins (XIV) (Scheme 2).

In harmony with the Brown method, NaBH_4 was added to the reaction mixture immediately after the disappearance of the yellow color, which testified to the completion of the addition reaction of the mercury salt to the hydrocarbon. GLC analysis of the reaction products disclosed that they contain, besides the starting 3-carene, also β -4-caranol (IX) and α -terpineol (XI) in a 4.4:1 ratio. Besides the indicated alcohols, a small amount of trans-1,8-terpin (XIV) was isolated when the reaction products were chromatographed on silica gel, which was identified by comparing with the authentic product, obtained from cis-terpin as described in [9]. In one of the experiments, apparently due to incomplete hydrogenolysis, we obtained a crystalline product with the composition $\text{C}_{12}\text{H}_{20}\text{HgO}_3$, which corresponded to the adduct: 3-carene- $\text{Hg}(\text{OAc})(\text{OH})$. In the IR spectrum of this adduct are present absorption bands that correspond to a trisubstituted

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Scheme 2

double bond ($1670, 3020 \text{ cm}^{-1}$), an ionized acetate group ($1600, 1340 \text{ cm}^{-1}$), and a tertiary OH group ($1105, 3350 \text{ cm}^{-1}$). Consequently, the mercury compound has the structure of the addition product to the cyclopropane ring (X). The same structure must be assigned to the hydroxymercury chloride that is isolated when the hydroxymercuration products are treated with NaCl, since the demercuration of the chloride with NaBH_4 gives only α -terpineol. The product of the hydroxymercuration of 3-carene at the double bond (VIII) was not isolated. On the basis of these data it is possible to assume that it is less stable. Testifying to the different stability of the (VII) and (X) adducts is the change in the ratio of β -4-caranol and α -terpineol as a function of the length of the hydroxymercuration step. As was mentioned above, during demercuration, β -4-caranol predominates (4.4:1) in the mixture immediately after the first step; the composition of the mixture of alcohols after demercuration for 24 h is 1:1, while, when based on the GLC analysis data, β -4-caranol was absent in the mixture after 48 h. A similar instability of the hydroxymercuration products was observed in [6], which explained the decrease in the yields of the alcohols when the hydroxymercuration period was prolonged.

As a result, the data of studying the hydroxymercuration-demercuration reaction show that 3-carene adds the mercury salt to both the double bond and the cyclopropane ring. It is possible to assume that, together with the double bond, the cyclopropane ring is also attacked under the reaction conditions of acetylation with mercuric acetate. Preferential attack of the double bond makes more probable the mechanism of forming *p*-menthadienol acetates (III) and (VII) via the intermediate allylic mercuriacetates [1], but the possibility of also forming them according to Scheme 1 is not excluded.

EXPERIMENTAL

The melting points were determined on a Kofler block. The IR spectra were taken on a UR-10 instrument. Analysis by the gas-liquid chromatography (GLC) method was run on a Khrom-2 chromatograph, using nitrogen as the carrier gas, refractory brick as the solid support, 10% poly(ethylene glycol adipate) as the stationary phase, and a temperature of $140\text{--}144^\circ\text{C}$.

Hydroxymercuration-Demercuration of 3-carene. To a suspension of 10 g of mercuric acetate in aqueous THF (31 ml of THF, 31 ml of H_2O) was added 4.4 g of 3-carene. When the yellow color had disappeared an alkaline solution of NaBH_4 (1.2 g of NaBH_4 , 1 g of NaOH, 31 ml of H_2O) was added to the reaction mixture in drops. The solution was decanted from the deposited metallic mercury (4.8 g, 77%), extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4 . Removal of the solvents gave a residue that was a mixture of an oil and white crystals. The filtered crystals had mp 185°C . Found: C 34.65; H 4.98; Hg 48.88%. $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Hg}$. Calculated: C 34.9; H 4.80; Hg 48.62%. Infrared spectrum (ν , cm^{-1}) (Nujol): 700, 930, 950, 1020, 1060, 1105, 1140, 1250, 1340, 1600, 3020, 3350. When 2.3 g of the oil was chromatographed on SiO_2 (30 g) we isolated 0.7 g of 3-carene (petroleum ether used as eluant); the fractions (0.1 g) that were eluted with benzene contained an alcohol that, based on the GLC analysis data and the IR spectra, was identical with α -terpineol. In the products of the fraction (0.1 g) that was eluted with a 1:1 mixture of benzene and ether was present β -4-caranol with mp 70°C , whose *p*-nitrobenzoate

had mp 142–144°C. The mixed melting point with the authentic β -4-caranol p-nitrobenzoate (mp 143–144°C) [10] was not depressed. The fraction (0.01 g) that was eluted with ethanol contained a product with mp 154–155°C, the mixed melting point (155–156°C) of which with the trans-1,8-terpin reported in [9], with mp 155–156°C, was not depressed.

In order to obtain more of the alcohol, having the same retention time as α -terpineol, the experiment on the hydroxymercuration–demercuration of 3-carene was run with larger amounts of the reactants: 50 g of $\text{Hg}(\text{OAc})_2$, 22 g of 3-carene, 150 ml of THF, 5 g of NaBH_4 , 5 g of NaOH , and 150 ml of H_2O . From 20.8 g of the reaction products by chromatographing on SiO_2 (150 g) we isolated 3.56 g of alcohols, which were separated by preparative TLC. We obtained 0.26 g of a substance with n_D^{20} 1.4830 and d_4^{20} 0.9320 (from [11], for α -terpineol, n_D^{20} 1.4805 and d_4^{20} 0.927). Infrared spectrum (ν , cm^{-1}): 800, 920, 935, 950, 1115, 1145, 1160, 1230, 1380, 1450, 1670, 3025, 3400; the p-nitrobenzoate had mp 137–139°C, and its mixed melting point with authentic α -terpineol p-nitrobenzoate was not depressed.

To a suspension of 10 g of $\text{Hg}(\text{OAc})_2$ in aqueous THF (31 ml of THF, 31 ml of H_2O) was added 4.3 of 3-carene in drops. The reaction mixture was allowed to stand at room temperature for approximately 36 h. The obtained white crystalline precipitate of the mercury salt (3.6 g, mp 224°C) was filtered. The filtrate was extracted with benzene. Evaporation of the benzene extract left a residue that was unreacted 3-carene. The aqueous layer from the benzene extraction was evaporated and then salted out with NaCl solution. The obtained hydroxymercury chloride (3.1 g, mp 149–153°C) was filtered.

Demercuration of Hydroxymercury Chloride. To a solution of 3.1 g of the hydroxymercury chloride in 20 ml of THF was added an alkaline solution of sodium borohydride (0.3 g of NaOH , 0.3 g of NaBH_4 , and 10 ml of H_2O). Heating up was observed and the appearance of metallic mercury (1.05 g; 64%). The reaction mixture was extracted with ether and the solvents were distilled off. The residue (0.4 g; 33%; n_D^{20} 1.4865), after preparative TLC on SiO_2 in the system: hexane–ethyl acetate (85:15), gave a product with n_D^{20} 1.4868 and, based on the GLC analysis data and the IR spectra (ν , cm^{-1}): 800, 925, 950, 1115, 1135, 1160, 1225, 1300, 1385, 1450, 1680, 3035, 3400, was identical with α -terpineol; the p-nitrobenzoate had mp 137–139°C, and its mixed melting point with α -terpineol p-nitrobenzoate (mp 139–140°C) was not depressed.

CONCLUSIONS

It was found that $\text{Hg}(\text{OAc})_2$ adds to 3-carene both to the double bond and to the three-membered ring; the formation of β -4-caranol and trans-1,8-terpin as demercuration products is in agreement with the trans-addition of the mercury salt to the double bond.

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