# STRUCTURES OF UNSATURATED ACETIC ESTERS FORMED

## IN THE REACTION OF 2-PINENE OXIDE WITH ACETIC ANHYDRIDE

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In previous communications [1-3] we have reported that in the action of acetic anhydride on 2-pinene oxide, apart from campholenaldehyde and sobrerol acetate, a mixture of acetates of unsaturated mono- and bi-cyclic alcohols of composition  $C_{12}H_{18}O_2$  is formed. It must be considered that the bicyclic acetic ester most probably has the structure of trans- or cis-pinocarveol acetate.



However, the identification of the alcohol-the product of the hydrolysis of the bicyclic acetate-with pinocarveol was not rigorously established [3]. While the constants of the alcohol were very close to those of (-)-trans-pino-carveol, not all of its crystalline derivatives were found to be characteristic for this substance. Also, the question of the nature of the monocyclic acetates has not been finally resolved. One of them, whose hydrolysis product gave (+)-carvone on oxidation with chromic anhydride, would be expected to be (+)-trans-carveol acetate. However, in its crystalline derivatives the product of the hydrolysis of this acetate was found to differ from (+)-trans-carveol. These contradictions in the data on the mono- and bi-cyclic acetates arise from their lack of homogeneity. The present work was undertaken with the object of clarifying the position.

We have shown [3] that, apart from pinocarveol acetate, in the reaction of 2-pinene oxide with acetic anhydride bornenol acetate may be formed, but the difference between the constants and the crystalline derivatives of the bornenol described in [4] and those for the bicyclic acetal under investigation indicates that the structure of bornenol acetate must be rejected. A second possible hypothesis—that the bicyclic acetate is a mixture of these two compounds—was not confirmed by chromatographic and spectroscopic results. Although in the chromatography of the bicyclic acetate several unexpected results were obtained, on the basis of them it can nevertheless be concluded that the bicyclic acetate is probably structurally homogeneous. In the chromatography process most of the acetate was hydrolyzed, and the hydrolysis product obtained in this way was identical to the product of the hydrolysis of the acetate with an aqueous alcoholic solution of sodium hydroxide. The acetate isolated from the chromatographic column did not differ from the original substance either in its constants or in its infrared (Fig. 1) and



Fig. 1. Infrared spectrum of bicyclic acetate.

Raman spectra. The infrared spectrum, which contained bands characteristic for the  $H_2C = C$  group at 1641 cm<sup>-1</sup>  $[\nu(C=C)]$  and 903 cm<sup>-1</sup> [ $\delta(C-H)$ ], confirmed the pinocarveol acetate structure. However, analysis of the Raman spectrum of the bicyclic acetate did not yield a definite conclusion. The spectrum contained two intense bands at 1629 and 1650 cm<sup>-1</sup>; on the one hand, these may be assigned to the  $\nu(C=C)$  vibrations of the  $CH_2=C$  and -CH=CHgroups respectively, and on the other hand this doublet can be regarded as characteristic for the spectrum of pinocarveol acetate on analogy with the spectra of nopol and myrtenol [5], which also contain doublets in the  $\nu(C=C)$  region at  $1648-1662 \text{ cm}^{-1}$  and  $1656-1671 \text{ cm}^{-1}$ . For comparison we determined the Raman spectrum of trans-pinocarveol (see Experimental)-the product of the isomerization of 2-pinene oxide with lithium diethylamide [6]. In the  $\nu(C=C)$  region of this spectrum only one band (1647 cm<sup>-1</sup>) was found. Since the identification of the unsaturated bicyclic acetate amounted to the identification of the corresponding alcohol, it was decided to isolate the latter in the pure state via a crystalline derivative. At about this time we had completed our study of the isomerization of 2-pinene oxide with lithi-

um diethylamide [6], and we found that in its constants the isomerization product was identical to the product of the hydrolysis of the bicyclic acetate obtained in the reaction of 2-pinene oxide with acetic anhydride. The isomerization product was found to be a mixture of (-)- and  $(\pm)$ -trans-pinocarveols. The (-)- and  $(\pm)$ -trans-pinocarveols isolated from the product of the hydrolysis of the bicyclic acetate via the corresponding 3,5-dinitrobenzoates had the same constants and gave the same crystalline derivatives as those isolated from the product of the isomerization of 2-pinene oxide; their infrared spectra were identical (Figs. 2 and 3).

It was found, therefore, that the unsaturated bicyclic acetate is a mixture of (-)- and  $(\pm)$ -trans-pinocarveol acetates. It appeared reasonable to suppose that the monocyclic acetates are also mixtures of optical active and racemic forms. We have already found [3] that the product of the hydrolysis of one of the monocyclic acetates gives (+)-carvone on oxidation with chromic anhydride; the hydrolysis product therefore contains (+)-carveol. The crystalline derivatives prepared earlier [3] for the product of the hydrolysis of this acetate are characteristic for  $(\pm)$ -transcarveol. By the fractional crystallization of large amounts of the 3,5-dinitrobenzoate of the product of the hydrolysis of the monocyclic acetate we obtained the 3,5-dinitrobenzoates of (±)-trans-carveol (m. p. 119.5-121°) and (+)trans-carveol (m. p. 108-110.5°). Comparison of the product of the hydrolysis of the 3,5-dinitrobenzoate of m. p. 108-110.5° with  $(\pm)$ -trans-carveol [7] showed that the former contained only 60% of  $(\pm)$ -trans-carveol. Moreover, in the value of  $[\alpha]_{D}$  it differed little from the product of the hydrolysis of the acetate [3]; when it was treated with p-nitrobenzoyl chloride the p-nitrobenzoates of (+)- and  $(\pm)$ -trans-carveols were obtained.  $(\pm)$ -trans-Carveol was also not obtained free from (+)-trans-carveol; moreover, a very small difference in the melting points of the hydrolyzed 3,5-dinitrobenzoates results from an appreciable difference in the content of impurities. Thus, a 3,5-dinitrobenzoate hydrolysis product of m. p. 119.5-121° contains 5.5% of (+)-trans-carveol [7], whereas the content of the latter in a hydrolysis product of somewhat lower melting point (118-120°) is already 18%. The infrared spectra of 3,5-dinitrobenzoate hydrolysis products of m. p. 108-110.5° and 119.5-121° are identical (Figs. 4 and 5). To these circumstances must be attributed the difficulty of identifying both the mono- and the bi-cyclic alcohols and their acetates formed in the reaction of 2-pinene oxide with acetic anhydride.

We briefly characterized the structure of the third product of composition  $C_{12}H_{18}O_2$ —the unsaturated monocyclic acetate—in a previous paper [3], but did not finally establish it. A possible structure for this monocyclic acetate is that of p-mentha-4(8),6-dien-2-ol acetate (V), which results from the stabilization of the carbocation (III) in the direction (2) with elimination of the proton from C-4. One of the ways in which we planned to prove the structure of the acetate consisted in converting it via the alcohol and tosylate into the corresponding hydrocarbon, which would not be difficult to identify from its crystalline derivatives. Unfortunately, we did not obtain the tosylate despite numerous attempts to synthesize it under various conditions. The infrared spectrum of the acetate (Fig. 6) contains no absorption band in the  $\nu(C=C)$  region; the band at 816 cm<sup>-1</sup>, which could be assigned to  $\delta(C-H)$ 



Fig. 2. Infrared spectrum of (-)-trans-pinocarveol.



Fig. 3. Infrared spectrum of (±)-trans-pinocarveol.

at a trisubstituted double bond, is of low intensity. The Raman spectrum of the acetate contains an intense band at 1677 cm<sup>-1</sup> characteristic for tri- and tetra-substituted double bonds and a band at 1647 cm<sup>-1</sup> of very low intensity. Further data on the positions of the double bonds in the molecule of the acetate might be obtained from an analysis of the spectra of the product of the oxidation of the corresponding alcohol. Actually, if the acetoxy, and therefore the hydroxy, group is in the allyl position, then in the  $\nu(C=O)$  region of the infrared spectrum of the product of the oxidation of the aband at about 1682 cm<sup>-1</sup>, characteristic for a cyclohexenone C=O group conjugated with the double bond. The conjugation with the C=O group should, in its turn, alter the position of the band due to the same double bond in the spectrum of the acetate [8]. In oxidation with manganese dioxide the alcohol from the acetate gave a very low yield (about 10%) of a product which was found to be a complex mixture. According to the infrared spectrum (Fig. 7), an aromatic compound predominates in the mixture (bands at 817, 1510, 1603, 1624, and 1666 cm<sup>-1</sup>). The high intensity of the band at 1666 cm<sup>-1</sup>, as compared with the band in the spectrum of cymene, is probably due to the superposition of the band at 1666 cm<sup>-1</sup>, as compared with the band in the spectrum of cymene, is probably due to the superposition of the band at 1666 cm<sup>-1</sup>, as compared with the band in the spectrum of cymene, is probably due to the superposition of the band due to the C=O group of an unsaturated ketone. The oxidation product forms a semicarbazone and a 3,5-dinitrobenzoate, which we were unable to identify because of their small amounts.



#### EXPERIMENTAL

Raman spectra were determined with an ISP-51 spectrograph with the 4358 A blue line from a mercury lamp as exciting radiation.

Action of Acetic Anhydride on 2-Pinene Oxide. 2-Pinene oxide [310 g, b. p. 73° (11 mm);  $n_D^{20}$  1.4680;  $\alpha_D$  +61.10°] was added dropwise in the course of 30 min to boiling acetic anhydride. The reaction mixture was then cooled, and acetic anhydride was vacuum-distilled off [b. p. 38-42° (11 mm)]. By repeated fractionation of the residue through a column of 17-plate efficiency we isolated three products of composition  $C_{12}H_{18}O_2$  (each in the form of several fractions with close constants).

I-b. p. 74-75.5 (1.5 mm);  $n_D^{20}$  1.4760-1.4766;  $d_4^{20}$  0.9916-0.9923,  $[\alpha]_D$  8.3-10.6°; yield 7%.



Fig. 7. Infrared spectrum of the product of the oxidation of the monocyclic alcohol.

Raman spectrum  $(\nu, \text{ cm}^{-1})$ : 208 (2), 278 (1), 338 (3), 320 (0), 403 (1), 465 (1), 492 (3), 600 (2), 623 (2), 654 5), 672 (1), 784 (2), 823 (4), 872 (4), 907 (4), 931 (2), 944 (2), 974 (1), 1022 (2), 1058 (3), 1107 (1), 1146 (5), 1187 (5), 1208 (2), 1227 (3), 1265 (2), 1323 (2), 1412 (4), 1440 (3), 1458 (2), 1467 (0), 1629 (6), 1650 (8), 1737 (2), 2868 (5), 2905 (5), 2933 (10), 2986 (6), 3080 (2).

II-b. p. 88-90° (3 mm);  $n_D^{20}$  1.4748-1.4757;  $d_4^{20}$  0.9706-0.9718;  $[\alpha]_D$  87.3-95.4°; yield 7%.

Raman spectrum ( $\nu$ , cm<sup>-1</sup>): 174 (2), 195 (1), 233 (2), 289 (2), 323 (3), 351 (2), 377 (1), 433 (2), 471 (1), 492 (1), 528 (1), 560 (3), 596 (2), 629 (3), 782 (4), 834 (6), 891 (1), 914 (7), 951 (0), 1018 (1 b), 1049 (3), 1097 (1), 1117 (1), 1165 (2), 1329 (4), 1377 (7), 1434 (7), 1442 (2), 1645 (8), 1675 (10), 1732 (3), 2835 (3), 2860 (4), 2880 (4), 2913 (7), 2936 (7), 2967 (4), 2984 (3), 3014 (2), 3079 (2).

III-b. p. 78-79° (1 mm);  $n_D^{20}$  1.4840-1.4848;  $d_4^{20}$  0.9807-0.9816;  $[\alpha]_D$  17.6-18.1°; yield 3%. Found C 74.23; H 9.40%. C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>. Calculated: C 74.19; H 9.34%.

Raman spectrum ( $\nu$ , cm<sup>-1</sup>): 179 (1), 254 (1), 319 (1), 362 (1), 422 (2), 449 (1), 492 (1), 516 (2), 577 (2), 639 (2), 663 (2), 705 (1), 760 (2), 793 (1), 830 (2), 911 (2), 933 (0), 967 (2), 1003 (1), 1022 (1), 1049 (1), 1072 (1), 1107 (0), 1125 (1), 1177 (1), 1191 (0), 1222 (7), 1272 (1), 1316 (1), 1347 (3), 1381 (7), 1426 (5), 1452 (5), 1647 (1), 1677 (10), 1736 (3), 2816 (4), 2855 (8), 2931 (10 b), 2977 (4).

For a mixture of (-)- and  $(\pm)$ -trans-pinocarveols-the product of the isomerization of 2-pinene oxide with lithium diethylamide [6]:

Raman spectrum ( $\nu$ , cm<sup>-1</sup>): 342 (3), 376 (1), 471 (2), 493 (2), 654 (8), 684 (2), 721 (0), 773 (4), 824 (4), 833 (4), 866 (4), 891 (4), 925 (4), 948 (1), 1027 (0), 1052 (4), 1086 (1), 1110 (1), 1143 (4), 1186 (4), 1205 (3), 1227 (3), 1265 (2), 1410 (2), 1440 (2), 1456 (2), 1647 (8), 2868 (7), 2929 (10 b), 2979 (10), 3072 (5).

Hydrolysis of the Acetate of B. p.  $74-75.5^{\circ}(1.5 \text{ mm})$ . The acetate (22.3 g) was hydrolyzed by heating it with 3.5% aqueous-alcoholic NaOH for 30 min in a water bath at 80°. The cooled reaction mixture was diluted with water and extracted with ether. Ether was removed, and distillation of the residue gave 16.7 g (96%) of product; b. p. 69-71.5° (3.5 mm);  $n_D^{20}$  1.4990.

3,5-Dinitrobenzoates of the Product of B. p.  $69-71.5^{\circ}(3 \text{ mm})$ . 16.7 g of the hydrolysis product and then 50 ml of dry pyridine were added with vigorous stirring to a solution of 28 g of 3,5-dinitrobenzoyl chloride in 360 ml of benzene. After three days at room temperature the reaction mixture was treated in the usual way. We isolated 8.7 g (22.8%) of a 3,5-dinitrobenzoate of m. p. 122-123.5° and 6.4 g (16.8%) of a 3,5-dinitrobenzoate of m. p. 96-98°.

<u>Hydrolysis of the 3,5-Dinitrobenzoate of M. p. 122-123.5°.</u> A solution of 8.7 g of the 3,5-dinitrobenzoate and 2.1 g of potassium hydroxide in 140 ml of ethanol and 25 ml of water was heated in a water bath for 30 min. The hydrolysis product had the constants: b. p. 69-70° (3 mm);  $n_D^{20}$  1.4993;  $d_4^{20}$  0.9785;  $[\alpha]_D$ -65.2:; yield 81%. p-Nitrobenzoate, m. p. 91-92°, undepressed by admixture of the p-nitrobenzoate of (-)-trans-pinocarveol [6].

<u>Hydrolysis of the 3,5-Dinitrobenzoate of M. p. 96-98</u>°. The 3,5-dinitrobenzoate (6.4 g) was hydrolyzed with a 2% aqueous-alcoholic solution of potassium hydroxide by heating the mixture for 90 min in a water bath at 65-70°. Constants of hydrolysis product: b. p. 68.5-70° (3.5 mm);  $n_D^{20}$  1.4989;  $d_4^{20}$  0.9780;  $[\alpha]_D$  -3.1°; yield 78%.

<u>p-Nitrobenzoates</u> from the Hydrolysis Product of B. p.  $68.5-70^{\circ}$  (3.5 mm). From 0.5 g of the hydrolysis product of b. p.  $68.5-70^{\circ}$  (3.5 mm) and 0.8 g of p-nitrobenzoyl chloride we obtained, after the first crystallization from petroleum ether, 0.3 g of a p-nitrobenzoate of m. p.  $69-70.5^{\circ}$  and 0.2 g of a p-nitrobenzoate of m. p.  $96-97.5^{\circ}$ . The first melted without depression in admixture with the p-nitrobenzoate obtained earlier [3] from the alcohol obtained by hydrolyzing the bicyclic acetate. However, after a second and subsequent crystallizations from the same solvent this p-nitrobenzoate had m. p.  $95-97^{\circ}$  and was found to be identical to the second p-nitrobenzoate of m. p.  $96-97.5^{\circ}$ .

Chromatography of the Acetate of B. p. 74-75.5° (1.5 mm). 13.4 g of the acetate was passed through a column containing 50 g of alumina of activity (III). Elution with a 1:1 mixture of petroleum ether (40-60°) and benzene gave 2 g of a product with b. p. 74-76° (2 mm);  $n_D^{20}$  1.4761;  $\alpha_D$  +9.75°; and elution with a 9:1 mixture of ether and methanol gave 6 g of a product with b. p. 65-67° (2 mm);  $n_D^{20}$  1.4993;  $\alpha_D$  -32.2°. 3,5-Dinitrobenzoate, m. p. 122-123.5°.

<u>Hydrolysis of the Acetate of B. p. 88-90° (3 mm).</u> 26.7 g of the acetate was hydrolyzed with a 2% solution of KOH in ethanol by heating the mixture for 2 h at 60-65°. The yield of the hydrolysis product was 96.5%; b. p. 94.5-95.5° (4 mm);  $n_D^{20}$  1.4951;  $\alpha_D$  +104.4°.

<u>3,5-Dinitrobenzoates of the Product of B. p. 94.5-95.5° (4 mm)</u>. From 12 g of the product and 25 g of 3,5dinitrobenzoyl chloride we obtained 8.5 g (31.1%) of a 3,5-dinitrobenzoate of m. p. 108-110.5° and 6 g (22%) of a 3,5-dinitrobenzoate of m. p. 119.5-121°.

Hydrolysis of the 3,5-Dinitrobenzoate of M. p. 108-110.5°. A solution of 2 g of potassium hydroxide in 60 ml of 90% ethanol was added to a heated solution of 8.5 g of the 3,5-dinitrobenzoate in 200 ml of ethanol. The solution

was boiled for 15 min, cooled, diluted with water, and extracted with ether. By distilling the residue remaining after the removal of solvents we obtained 2.2 g (60%) of a product with b. p. 82-83° (4 mm);  $n_D^{20}$  1.4950;  $d_4^{20}$  0.9511;  $[\alpha]_D$  +126°.

<u>p-Nitrobenzoate of the Product of B. p. 82-83° (4 mm).</u> 0.5 g of the product of b. p. 82-83° (4 mm) and then 5 ml of pyridine were added to a solution of p-nitrobenzoyl chloride in 10 ml of benzene. After 5 h the reaction mixture was diluted with ether, washed with dilute hydrochloric acid and water, and dried with sodium sulfate. The residue remaining after the removal of solvents immediately crystallized. A solution of the product in petroleum ether was filtered to remove the undissolved part (0.1 g, m. p. about 200°). The solution was cooled with ice, and 0.2 g of a p-nitrobenzoate of m. p. 99-101° separated (m. p. after recrystallization 100-102°); from the filtrate after partial evaporation at room temperature we also isolated 0.2 g of a p-nitrobenzoate of m. p. 75-82°; after three crystallizations from petroleum ether the p-nitrobenzoate had m. p. 76-78°.

<u>3,5-Dinitrobenzoate of the Product of B. p. 82-83° (4 mm)</u>. By treating 0.3 g of the product with 0.5 g of 3,5dinitrobenzoyl chloride in a mixture of benzene and pyridine we obtained 0.3 g of a mixture of 3,5-dinitrobenzoates, which were separated into two 3,5-dinitrobenzoates by fractional crystallization from petroleum ether: 1) m. p. 110-112°;  $[\alpha]_D$  236.8° (c 4.11, benzene), and 2) m. p. 120-121°.

Hydrolysis of the 3,5-Dinitrobenzoate of M. p. 119.5-121°. A solution of 6 g of the 3,5-dinitrobenzoate and 1.5 g of potassium hydroxide in 150 ml of 85% ethanol was heated at 60-70° for 40 min. After the usual treatment of the reaction mixture we obtained 2.1 g (90%) of product; b. p. 84.5° (3.5 mm);  $n_D^{20}$  1.4953;  $d_4^{20}$  0.9501;  $[\alpha]_D$  +11.9°. 3,5-Dinitrobenzoate, m. p. 120-121°;  $[\alpha]_D$  0°.

Hydrolysis of the Acetate of B. p. 78-79° (1.5 mm). A solution of 10.4 g of the acetate and 5 g of potassium hydroxide in 170 ml of 85% ethanol was heated in a water bath for 3 h. The yield of hydrolysis product was 88.4%; b. p. 94° (4 mm);  $[\alpha]_D$  +50.2° (c 1.99, ethanol). The product solidified immediately after distillation. Found: C 78.72; H 10.48%. C<sub>10</sub>H<sub>16</sub>O. Calculated: C 78.90; H 10.59%. 3,5-Dinitrobenzoate, m. p. 138-139°. Found: C 58.84; H 5.21%. C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>N<sub>2</sub>. Calculated: C 58.95; H 5.20%.

Oxidation of the Product of B. p. 94 (4 mm). Manganese dioxide prepared by the procedure given in [9] was added in three portions with stirring to a solution of 7.2 g of the product in 200 ml of CCl<sub>4</sub>; only a slight rise in temperature of the reaction mixture was observed. The reaction mixture was stirred for 6 h at 40° and then steam-distilled, and the distillate was extracted with ether. The residue remaining after the removal of ether was distilled: b. p. 102-110° (11.5 mm);  $n_D^{20}$  1.5180;  $d_4^{20}$  0.9679;  $[\alpha]_D$  +8.5°; yield 10.5%. Found: C 80.97; 80.98; H 9.42; 9.37%.  $C_{10}H_{14}O$ . Calculated: C 79.95; H 9.39%. Semicarbazone, m. p. 221-222°. 3,5-Dinitrobenzoate, m. p. 115-120° (after one crystallization from ethanol).

### SUMMARY

The bicyclic acetate obtained in the reaction of 2-pinene oxide with acetic anhydride is a mixture of (-)and  $(\pm)$ -trans-pinocarveol acetates; one of the monocyclic acetates obtained is a mixture of (+) and  $(\pm)$ -trans-carveol acetates.

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