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OXIDATION OF 3-CARENE BY THALLIUM(III) ACETATE

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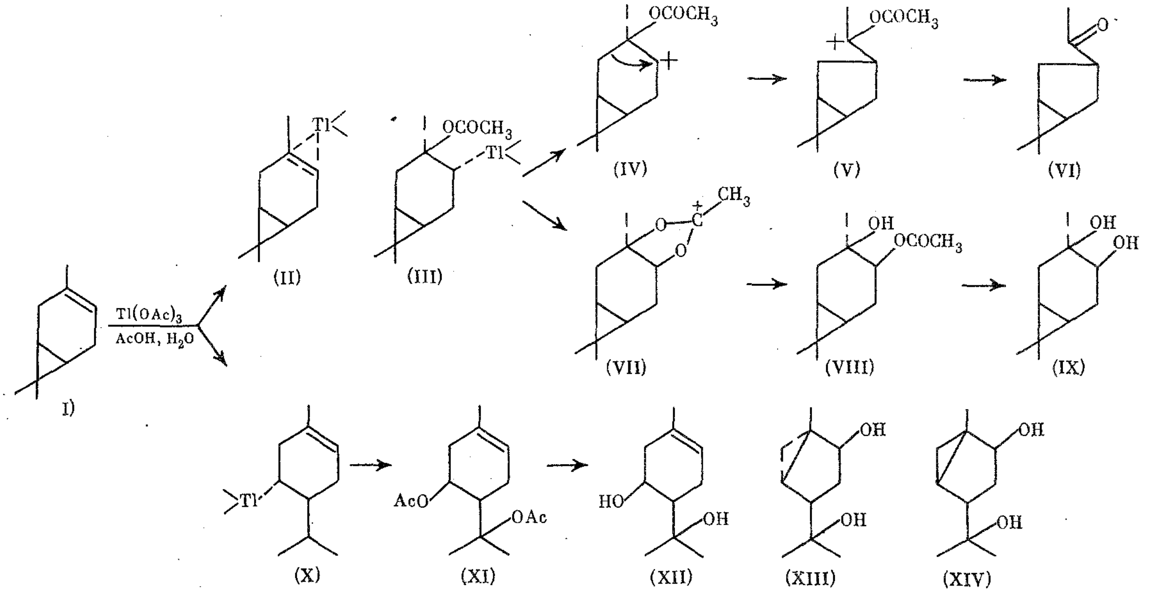
In the reaction of 3-carene (I) with $Pb(OAc)_2$ and $Hg(OAc)_2$, the double bond is preferentially attacked, and products of allyl oxidation are formed [1-4]. In [4] it was shown that $Hg(OAc)_2$ also adds to the cyclopropane ring of 3-carene. Thallium(III) acetate, which in reactivity as an electrophilic reagent is intermediate between Pb(IV) and Hg(II) acetates, can add both to the double bond and to the cyclopropane ring [5, 6]. It was interesting to study its action on 3-carene (I), in particular, because the oxidation of (I) by Tl(III) nitrate leads to a single product of attack at the double bond, with subsequent skeleton rearrangement, i.e., 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane [7].

In the present work we present data on the transformations of (I) under conditions of reaction with Tl(III) acetate. In saponification products of the reaction mixture, 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane (VI) [8], 2-(p-tolyl)-2-propanol [1], and 3β,4β-caranediol (IX) [9] were found (see scheme 1). A diol with composition $C_{10}H_{18}O_2$, mp 70-72°C and a product mp 152-153.5°C were also isolated.

From the IR and PMR spectral data, the structure of 1-(p-menthene)-5,8-diol (XII) was established for the diol, mp 70-72°C. According to the PMR spectrum, the structure of the diol includes fragments $(CH_3)_2-C-O-$, $CH_3-C=C$, $-CH-O$, $HC=C$, and OH. The IR spectrum contains absorption bands of trisubstituted double bonds, and secondary and tertiary OH groups.

In the IR spectrum of a 10^{-3} M solution of (XII) in CCl_4, in the stretching vibrations region of the OH group, there is an intense band at 3523 cm^{-1} and less intense bands at 3573, 3603, and 3621 cm^{-1}. The last

Scheme 1



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band corresponds to a tertiary hydroxyl which is a proton acceptor. Since the bands of the free secondary hydroxyl were not observed in the IR spectrum, the 3523 cm^{-1} band can be assigned to the secondary OH proton donor [10], and the 3573 cm^{-1} band to the stretching vibrations of a secondary hydroxyl, which is a proton donor in the H bond with π-electrons. An examination of Dreiding models for (XII) with a half-chair conformation for the six-membered ring showed that the intramolecular H-bond can arise at both cis- and trans-diequatorial positions of the OH and hydroxyisopropyl groups. But in the last case, because of large distances, the H-bond with the double bond π-electrons cannot be formed, so that these substituents most probably are present in the cis-position, and the secondary OH group is axial [10].

The mass spectrum of (XII) agrees with the structure proposed for this compound. The absence of a molecular ion peak in the spectrum indicates the low stability of this ion, which is characteristic of molecular ions of tertiary alcohols. The presence of two hydroxyl groups in (XII) is confirmed by signals of $[M - H_2O]^+$ at 152(5.1) and $[M - H_2O]^+$ at 134(2.8), and of the hydroisopropyl group by a signal with m/z 59(64).

According to the mass spectrum data, the compound with the composition $C_{10}H_{18}O_2$, mp 152-153.5°C contained two hydroxyl groups, as indicated by peaks of $[M - H_2O]^+$ at 152 (0.86) and $[M - 2H_2O]^+$ at 134(4.1), and a hydroxylisopropyl group with an intense peak with m/z 59(63). The peak of the molecular ion is practically absent in the spectrum. The PMR spectrum confirms the presence of the $(CH_3)_2-C-O$ group and indicates the absence of double bonds in this product. Its IR spectrum contained absorption bands of secondary and tertiary OH groups and a whole series of bands in the region where stretching vibrations of the $H-C=CH$ double bonds usually appear (3000, 3040, 3070 cm^{-1}). Although, according to the data of the PMR spectrum, this compound does not contain double bonds, these frequencies may indicate the presence of a cyclopropane ring in the compound. A similar picture is also observed in the IR spectrum of 1-methyl-4-(α-hydroxyisopropyl)-bicyclo[3.1.0]hexane-2-cis-ol (XIV) (3005, 3030, 3055, 3070 cm^{-1}) which also has no double bonds but contains a three-membered ring [11]. A comparison of the mass spectra of these compounds showed that they are similar: Both are characterized by the absence of a molecular peak, and the presence of intense peaks with m/z 94, 79, 59.

From these data it can be assumed that the product with mp 152-153.5°C contains a three-membered ring and a hydroxyisopropyl group, has the structure (XIII), and is probably a stereoisomer of (XIV). However, this requires additional verification. In the IR spectra of a 10^{-3} M solution of (XIII) in CCl_4 in the region of the stretching vibrations of the OH group, intense bands at 3465 and 3602 cm^{-1} and a shoulder at 3622 cm^{-1} are observed, which correspond to a tertiary hydroxyl, a proton acceptor. The band at 3602 cm^{-1} can be ascribed to the OH group bound to the cyclopropane ring, and the band at 3465 cm^{-1} to the stretching vibrations of the secondary hydroxyl, a proton donor in the H bond with the tertiary hydroxyl [12]. The possible paths of formation of the compounds identified are listed in Scheme 1.

Thallium(III) acetate can stereospecifically attack both the double bond and the three-membered ring in 3-carene. Compounds (VI) and (IX) are formed as the result of attack at the double bond. During the formation of (VI), a Wagner–Meerwein rearrangement takes place. Because of moisture in the medium, the acetoxonium cation (VII), formed as an intermediate product, transforms to 3β,4β-caranediol acetate (VIII). The acetate of 1-(p-menthene)-5,8-diol (XI) forms as the result of attack on the cyclopropane ring by the reagent.

Thus, in the 3-carene molecule both the double bond and the cyclopropane ring are subjected to attack by thallium(III) acetate.

EXPERIMENTAL

The IR spectra were run on the UR-10 apparatus, the PMR spectra on the Varian T-60 and Varian HA-100 apparatus, and the mass spectra on the MI-1305 mass spectrometer, fitted with a system for direct admission of the compound into the ionic source and a system for a rapid recording of the mass spectra at an ionizing voltage of 50 V, and an admission temperature of the sample of ~20°C. The sum of intensities of all peaks was taken as 100. The compounds were deuterated by mixing the sample with D_2O in the admission system, followed by evacuation of water in vacuo. The melting points were determined on a Koffler block. The GLC analysis was carried out on a Chrom-4 apparatus, using a column with 5% poly(ethylene glycol sebacate) on Chromosorb G, gas carrier N_2. For absorption chromatography, silica gel, brand Silicagel, Chemapol, and for thin-layer chromatography, Silufol plates were used. Thallium(III) acetate was obtained by the method in [12].

Oxidation of 3-Carene (I) by Thallium(III) Acetate. A 81.6 g portion of (I) was added dropwise to a solution of $Tl(OAc)_3$, prepared from 100 g of Tl_2O_3 and 700 ml of glacial acetic acid; the temperature of the reaction mixture was maintained at 27°C. The reaction mixture was left to stand for 3 days at 20°C, diluted with water, and extracted with ether. The ethereal extracts were washed with water, $NaHCO_3$ solution, and again with water, and were dried over $MgSO_4$. The ether was evaporated, and the unreacted (I) (50 g) was distilled from the residue (88.9 g). The reaction product (34.2 g) was further saponified by heating (6 h, 80°C) with an alcoholic solution of alkali (16.2 g NaOH in 80 ml of H_2O and 210 ml of ethanol). From the saponification product (10.63 g), 0.88 g of (I) were isolated by chromatography on SiO_2 (eluent – petroleum ether) and 0.84 g of (VI) (eluent – petroleum ether – ether, 9 : 1). IR spectrum, (ν, cm^{-1}): 800, 850, 1130, 1170, 1185, 1220, 1280, 1300, 1360, 1380, 1410, 1440, 1710, 2730, and 3010; 2,4-dinitrophenylhydrazone, mp 133-135°C (C_2H_5OH) did not depress the melting point when mixed with 2,4-dinitrophenylhydrazone of 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane [8].

On elution with a petroleum ether – ether mixture (7 : 3), 1 g of 2-(p-tolyl)-2-propanol was obtained. IR spectrum (ν, cm^{-1}): 820, 870, 960, 1100, 1140, 1170, 1260, 1360, 1380, 1510, 3020, 3050, 3090, 3400. PMR spectrum (δ, ppm): 1.5 s ($2CH_3CO$, 6H), 2.33 ($CH_3C_6H_4$, 3H), 7.01 q (C_6H_4, 4H).

3β,4β-Caranediol (IX) was obtained in a yield of 1.69 g from fractions eluted by a petroleum ether – ether mixture (4 : 6), mp 39-41°C. IR spectrum (ν, cm^{-1}): 870, 910, 990, 1060, 1090, 1120, 1170, 1240, 1270, 1380, 2730, 3000, 3400. The IR and PMR spectra of (IX) were identical with the corresponding spectra of 3β,4β-caranediol [9].

1-(p Menthene)-5,8-diol (XII). Diol (XII) was obtained in a yield of 0.61 g from fractions eluted by a petroleum ether – ether mixture (4 : 6), mp 70-72°C (petroleum ether), $[\alpha]_D$ −72.9° (C 1.41, C_6H_6). Found: C 70.11; H 10.73%. $C_{10}H_{18}O_2$. Calculated: C 70.6; H 10.59%. IR spectrum (ν, cm^{-1}, mineral oil): 800, 880, 910, 940, 950, 1050, 1075, 1140, 1170. PMR spectrum (δ, ppm): 1.08; 1.24 980, ($(CH_3)_2C-O$, 6H), 1.58 s ($CH_3C=C$, 3H), 4.26 s (OH, 2H), 4.38 (CHOH, 1H), 5.36 (HC=C, 1H). Mass spectrum of (XII) (m/z, relative intensity, %): 155 (0.6), 153 (0.9), 152 (5.1), 137 (12), 134 (2.8), 123 (1.9), 121 (2.3), 120 (1.7), 119 (13), 110 (12), 109 (100), 108 (18), 95 (16), 94 (47), 93 (2.7), 91 (20), 79 (81), 77 (19), 69 (11), 68 (16), 67 (17), 59 (64), 57 (16), 55 (15), 53 (14), 45 (14), 43 (66), 41 (44), 39 (20). Dehydration of (XII) (0.1 g) on heating (125-140°C) under N_2 with $KHSO_4$ (0.4 g), followed by oxidation of the product obtained by a solution of 1.85 g of CrO_3 in 4 ml of AcOH, 6.9 ml of H_2O and 2 ml of H_2SO_4, and esterification of the acid obtained by methanol with bubbling gaseous HCl, gave dimethyl terephthalate, mp 140-141°C, melting without depression of the melting point on mixing with an authentic sample.

Product $C_{12}H_{18}O_2$, mp 152-153.5°C (0.6 g), $[\alpha]_D$ −41.3° (C 1.21, C_2H_5OH) was isolated from fractions eluted with a petroleum ether – ether mixture (1 : 9). Found: C 70.39; H 10.70%. $C_{10}H_{18}O_2$. Calculated: C 70.6; H 10.59%. IR spectrum (ν, cm^{-1}) (mineral oil): 820, 830, 880, 930, 955, 980, 1025, 1040, 1080, 1100, 1155, 1170, 1190, 1220, 1230, 1280, 1380, 3000, 3040, 3070, 3400. PMR spectrum (δ, ppm, C_6H_6): 0.8; 0.32 (H at Δ); 1.1; 1.23; 1.4 ($3-CH_3$, 9H). Mass spectrum (m/z, relative intensity, %): 153 (0.14), 152 (0.86), 137 (4.3), 135 (0.86), 134 (4.1), 123 (0.6), 121 (0.6), 120 (1.0), 119 (11), 109 (11), 105 (3.7), 94 (60), 93 (26), 91 (29), 79 (100), 77 (30), 59 (63), 45 (14), 43 (59), 41 (24), 39 (20).

CONCLUSIONS

Oxidation of 3-carene by thallium(III) acetate leads to 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane; 2-(p-tolyl)-2-propanol; 3β,4β-caranediol, 1-(p-menthene)-5,8-diol, and a product with an assumed structure of 1-methyl-4-(α-hydroxyisopropyl)bicyclo[3.1.0]hexane-2-cis-ol.

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INFLUENCE OF RADICAL CENTER ON OXIDATIVE PROPERTIES OF NITRON GROUP IN REACTION OF NITROXYL RADICALS OF 3-IMIDAZOLINE 3-OXIDE WITH HYDRAZINE

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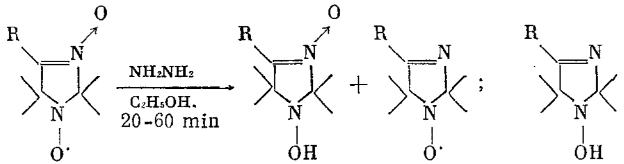
547.782 :546.171.5

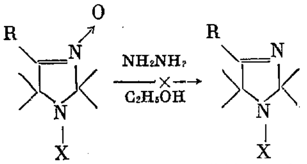
It is known [1, 2] that hydrazine and its derivatives are effective reducing agents of nitroxyl radicals to the corresponding hydroxylamines. During the study of the reduction of nitroxyl radicals of 3-imidazoline 3-oxide (I) by hydrazine hydrate in alcohol at 20°C, we found that in this reaction, besides the usual reduction of the radical center to the hydroxylamino group and formation of diamagnetic product (II), desoxygenation of the nitron group and formation of radical (III) occur in parallel, and radical (III) is further reduced to the diamagnetic product (IV)



(I a—h) (II a—h) (III a—h) (IV a—h) (1)

R = CH_3 (a); $i\text{-}C_3H_7$ (b); C_6H_5 (c); $p\text{-}FC_6H_4$ (d); $p\text{-}ClC_6H_4$ (e); $p\text{-}BrC_6H_4$ (f); $p\text{-}CH_3C_6H_4$ (g); $p\text{-}CH_3OC_6H_4$ (h).

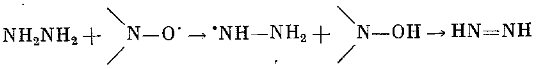
The reduction of the nitron group with the formation of product of type (III) takes place under these conditions in the case of the paramagnetic derivatives (I) only. In diamagnetic derivatives (V), with different groups at position 1 of the heterocyclic ring, under similar conditions there is no reduction of the nitron group



(V a, c) (VI a, c)

X = H, CH_3, NO

Hydroxylamines (II) also do not react with hydrazine in the absence of oxygen. In an alcoholic solution of hydrazine in an argon atmosphere, compound (II) does not change in the course of a month. In a normal atmosphere, where there is always the possibility of oxidation of compounds (II) into radicals (I) by dissolved atmospheric oxygen and the occurrence of process (1), (II) converts into radicals (III), which after 14 days were isolated in yields of 70-80%. This difference in behavior of the diamagnetic and paramagnetic derivatives of 3-imidazoline 3-oxide with respect to hydrazine is probably due to the fact that the nitron group becomes reduced not by the hydrazine itself, but by the products of its partial oxidation with better reducing properties, for example, by diimide [3]



$$NH_2NH_2 + {>}N{-}O^{\cdot} \rightarrow {}^{\cdot}NH{-}NH_2 + {>}N{-}OH \rightarrow HN{=}NH$$

However, when compounds (V) were held with hydrazine in the presence of nitroxyl radicals or Cu^{2+}, able to form diimide or other active particles, products of type (VI) did not form. Thus, the necessary condition for the

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