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Chemistry

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Abstract

Full Text

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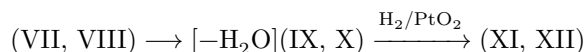
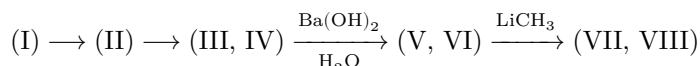
A New Synthesis of Phytol

(Presented by Academician B. A. Kazanskii, February 12, 1960)

In one of our preceding works ⁽¹⁾ we carried out the alkylation of dihydroresorcinol with prenyl bromides (II), and as a result obtained, in about 50% yield, a series of cyclic β -diketones containing isoprenoid chains.

In the present paper it is shown that these dihydroresorcinol derivatives can be used in the synthesis of phytol (XIII) and other isoprenoid compounds.

Reaction scheme



III, V, VII, IX, XI: $R = \text{CH}_3$; IV, VI, VIII, X: $R = \text{geranyl residue}$; XII: $R = \text{hexahydrofarnesyl residue}$
(XIII) phytol

In the hydrolytic cleavage of 2-prenyl- and 2-geranyldihydroresorcinols (III) and (IV), the corresponding keto acids (V) and (VI) were formed in high yields; these smoothly entered into reaction with an excess of methylolithium with the participation of both functional groups. Upon dehydration of the resulting keto alcohols (VII) and (VIII) with potassium bisulfate, followed by exhaustive hydrogenation of the unsaturated ketones (IX) and (X) over platinum oxide, the known ketones—tetrahydrogeranylacetone (XI) and hexahydrofarnesylacetone (XII) ⁽²⁾, previously synthesized by other methods—were isolated. According to ⁽³⁾ and the data of one of us ⁽²⁾, ketone (XII) can readily be converted into phytol (XIII).

Thus, we have developed a new method for the synthesis of isoprenoid compounds, which makes it possible to extend the chain of vinyl alcohols (I) by 8 carbon atoms and to obtain, in high yields, ketones of the type (XI) and (XII).

Experimental Part

Preparation of tetrahydrogeranylacetone (XI).

To a solution of methyllithium, prepared from 5.5 g (0.79 g-at.) of lithium, 56.3 g (0.39 mole) of methyl iodide, and 300 ml of anhydrous ether, with stirring, were added 15 g (0.07 mole) of 5-keto-9-methyl-8-decenoic acid (V) (m.p. 41–42°) in 150 ml of anhydrous ether. The reaction mixture was boiled for 1 h and then treated with ice. From the ether layer there were isolated 15 g of crude keto alcohol (VII), containing 98% carbonyl compound*.

A mixture of the obtained keto alcohol (VII) and 1 g of potassium bisulfate was heated in vacuo at 60 mm to 120°, and then for 20 min the temperature was raised to 160°. The dehydration product was diluted with ether, washed with water, and, after removal of the solvent, gave 10.7 g of unsaturated ketone (IX) with b.p. 107–112° at 7 mm and n_D^{20} 1.4705, containing 85% carbonyl compound.

Found %: C 80.36; 80.48; H 11.29; 11.53
 $C_{13}H_{22}O$. Calculated %: C 80.35; H 11.41

According to the literature data, geranylacetone has b.p. 133–135° at 20 mm and n_D^{20} 1.4664 (2).

On hydrogenation of 10.9 g of unsaturated ketone (IX) in methanol over platinum oxide (744 mm, 20°), two equivalents of hydrogen (2.7 l) were absorbed. As a result, 9.6 g of tetrahydrogeranylacetone (XI) were obtained, with b.p. 103–108° at 7 mm and n_D^{20} 1.4375, containing 84% carbonyl compound. The semicarbazone melts at 95–96° and gives no depression of the melting point with an authentic sample. In the literature (2), the following constants are given for tetrahydrogeranylacetone: b.p. 95–97° at 4 mm, n_D^{20} 1.4334, semicarbazone, m.p. 95–96°.

Preparation of hexahydrofarnesylacetone (XII).

To a solution of 350 g of barium hydroxide hydrate in 2 l of water were added 70 g (0.28 mole) of 2-geranyldihydroresorcinol (IV) (m.p. 101–104°) (1), and the mixture was boiled with stirring for 12 h. After cooling and acidifying with conc. HCl (to Congo), the reaction mixture was extracted with ether to give 54.4 g of 5-keto-9,13-dimethyl-8,12-tetradecadienoic acid (VI) with b.p. 181–184° at 0.05 mm, n_D^{20} 1.4833.

Found %: C 71.88; 72.24; H 9.84; 9.97
 $C_{16}H_{24}O_2$. Calculated %: C 72.14; H 9.84

The S-benzylthiuronium salt melts at 121–122° (from aqueous methanol).

Found %: N 6.87; 6.83
 $C_{24}H_{36}O_3N_2S$. Calculated %: N 6.48

Similarly, by the action of methyllithium (3.26 g (0.48 g-at.) of lithium and 33.4 g (0.23 mole) of methyl iodide) on 12.2 g (0.046 mole) of 5-keto-9,13-dimethyl-8,12-tetradecadienoic acid (VI) and subsequent dehydration of the keto alcohol (VIII), containing 97% carbonyl compound, 9.4 g of unsaturated ketone (X) were obtained, with b.p. 120-125° at 0.05 mm and n_D^{20} 1.4811, containing 90% carbonyl compound.

Found %: C 82.03; 82.29; H 11.66; 11.62
 $C_{18}H_{30}O$. Calculated %: C 82.38; H 11.52

According to the literature data (2), farnesylacetone has b.p. 143-144° at 0.42 mm and n_D^{20} 1.4810.

* Here and below, according to oximation data.

12.3 g (0.047 mole) of the unsaturated ketone (X) was hydrogenated in methanol over platinum oxide (738 ml, 20°). After the absorption of three equivalents of hydrogen (3.5 l), 12.1 g of hexahydrofarnesylacetone (XII) was isolated, b.p. 107-110° at 0.05 mm and n_D^{20} 1.4458, containing 88% of the carbonyl compound.

Found, %: C 80.80; 80.57; H 13.70; 13.56
 $C_{18}H_{36}O$. Calculated, %: C 80.52; H 13.52

The semicarbazone melts at 68-69° and gives no depression of the melting point with an authentic sample (m.p. 68-69°) (3). According to the literature data (2), hexahydrofarnesylacetone has the following constants: b.p. 120-123° at 1 mm, n_D^{20} 1.4445, semicarbazone, m.p. 69-70°.

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Note: Figure translations are in progress. See original paper for figures.

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