FREE-RADICAL ADDITION OF ALCOHOLS TO α , β -UNSATURATED KETONES AND TAUTOMERISM OF FORMED 4-HYDROXYKETONES

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4-Hydroxyaldehydes are formed in the free-radical addition of alcohols to α,β -unsaturated aldehydes, which under the reaction conditions are cyclized to 2-alkoxytetrahydrofurans [1]. In the case of the 5-hydroxyaldehydes, which are obtained in a similar manner from tetrahydrofurfuryl alcohol (THFA), the ratio of the open and cyclic forms is quite dependent on the steric factor [2]. In contrast to the 4-hydroxyaldehydes, the 4-hydroxyketones exist in both the cyclic (hemiacetal) and the open form [3]. The ring-chain tautomerism of the 4-hydroxyketones was studied on the example of compounds that contain a primary hydroxyl group [3].

In order to ascertain the effect of the structure of the hydroxyketones on the amount of the open and the cyclic form, in the present paper we obtained some 4- and 5-hydroxyketones that contain a primary, secondary or tertiary OH group. Their synthesis was accomplished by the free-radical addition of alcohols to methyl vinyl ketone and mesityl oxide, initiated by di-tert-butyl peroxide, under the conditions given in [1, 2]

Since in the free-addition reaction with olefins the methine group of THFA has a higher reactivity than the hydroxymethyl group [4], we were able to add THFA to mesityl oxide, which fails to add aliphatic alcohols under these conditions



The properties of the synthesized compounds are given in Table 1. Compounds (VII)-(X), which contain a secondary OH group, exist primarily in the cyclic hemiacetal form, the amount of which decreases with increase in the size of the alkyl substituent at the C atom attached to the OH group. The cyclization is made even more difficult if branching is present in the alkyl substituent [compound (VI)]. The open form predominates in the 4-hydroxyketones with a tertiary OH group [compounds (III)-(V)]. These facts indicate the important role of the steric effect in the cyclization step. The adduct of benzyl alcohol with methyl vinyl ketone (XI) was obtained as the cyclic acetal of 2-methyl-2-benzyloxy-5-phenyltetrahydrofuran. It is possible that in the given case, due to the high acidity of benzyl alcohol when compared with alignatic alcohols [5].

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TABLE 1

Com- pound No.	Yield, 🍕	Bp, °C (p, mm Hg	n _D ²⁰	Amount of open form,9%	Molár ab- sorption co- efficient	Foun	d, % н	Empiri- cal for- mula	Calcul c	ated, %
(I) (II) (III) (IV) (V) (VI) (VII) (VIII) (VIII) (IY)	25 48 10 15 30 25 25 25	$\begin{array}{c} 87 - 89 & (0,08) \\ 104 - 105 & (0,1) \\ 45 - 47 & (7) \\ 77 - 79 & (0,1) \\ 87 - 89 & (0,09) \\ 90 - 93 & (0,1) \\ 110 - 112 & (0,05) \\ 93 - 95 & (0,05) \\ 93 - 95 & (0,06) \end{array}$	1,4731 1,4730 1,4270 1,4331 1,4840 1,4505 1,4578 1,4482 1,4482 4,4490	100 100 100 100 70 65 45 30 35	246 250 245 248 170 157 106 73 85	65,94 62,97 64,36 71,73 73,76 72,18 73,10 72,23 71,56	9,87 8,70 10,54 11,82 9,90 11,82 12,31 12,15 12,15	$\begin{array}{c} C_{11}H_{20}O_8\\ C_9H_{16}O_3\\ C_7H_{14}O_2\\ C_{11}H_{22}O_2\\ C_{10}H_{18}O_2\\ C_{12}H_{24}O_2\\ C_{12}H_{24}O_2\\ C_{12}H_{24}O_2\\ C_{12}H_{24}O_2\\ C_{12}H_{24}O_2\\ C_{12}H_{24}O_2\\ C_{11}H_{22}O_2\\ C_{11}H_{22}O_2\\ \end{array}$	65,96 62,79 64,58 71,00 73,80 72,02 73,70 71,98 71,00	10,06 9,36 10,83 11,87 9,80 12,08 12,36 12,09 11,87
(\mathbf{X})	14	97—99 (15) 77—79 (0.06)	1,4172	10	23	$66,41 \\ 80,27$	11,43 7,64	$C_8H_{16}O_2 \\ C_{18}H_{20}O_2$	66,60 80,59	11,17 7,51

the intermediate hemiacetal is more easily protonated and then undergoes hydration to give the acetal.

5-Hydroxyketones (I) and (II) exist only in the open form. On the example of the adduct of methyl vinyl ketone and cyclohexanol (V) it was shown that the ratio between the open and cyclic forms is practically the same in CCl_4 , isooctane, acetonitrile or 1-butanol.

EXPERIMENTAL METHOD

The IR spectra were obtained on a UR-10 instrument, while the NMR spectra were taken on a Varian DA-IL-60 spectrometer. The GLC was run on a LKhM-8m chromatograph equipped with a 2-m column that was filled with 10% PEG (mol. wt. 6000) and 10% Siss Silicone deposited on Chromosorb W.

The free-radical addition reaction was run as described in [4], at 145-150°C and an alcohol-unsaturated ketone-di-tert-butyl peroxide mole ratio of 10:1:0.15, for 5 h. The yield of the 1:1 adducts increases up to 50-60% when the alcohol-methyl vinyl ketone ratio is raised to 40:1. The reaction was run in an autoclave in the case of the isopropyl and butyl alcohols. The 1:1 adducts were isolated from the reaction mass by vacuum-distillation. The conversion of the methyl vinyl ketone is close to 100%, and most of it enters into the composition of the high-boiling products. The purity of the adducts was checked employing the methods of IR spectroscopy, GLC and NMR.

Adduct (I) has: IR spectrum (ν , cm⁻¹): 1720 (C=O), 1050 and 3450 (primary OH); and NMR spectrum in CCl₄ (δ , ppm): singlets 0.9 (CH₃- $\overset{1}{C}$ -CH₃) and 2.0 (CH₃CO), with a 2:1 ratio of the intensities, and multiplets 1.76 and 3.43 (CH₂ groups of side chain and nucleus).

The amount of the open form was determined from the molar absorption coefficient of the 1720 cm⁻¹ band in the TR spectrum; this band is characteristic for the stretching vibrations of the C = O group. As the standard we used methyl hexyl ketone, for which the calibration curve, relating $\varepsilon_{C} = O$ to the molar concentration in CCl_4 , was obtained. The values of ε , given in Table 1 for each adduct, are the average of 3-4 measurements for CCl_4 solutions of approximately the same concentration (0.1-0.01 M).

CONCLUSIONS

1. Some 4- and 5-hydroxyketones were synthesized by the free-radical addition of alcohols to α,β -unsaturated ketones.

2. According to the data of the IR spectra, the 4-hydroxyketones exist in both the open and cyclic (hemiacetal) forms. The amount of the open form increases with increase in the steric hindrance in the cyclization step. The 5-hydroxyketones exist only in the open form.

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