IODOCYCLIZATION OF CIS-1-R-2-ALLYLCYCLOPENTAN-1-OLS

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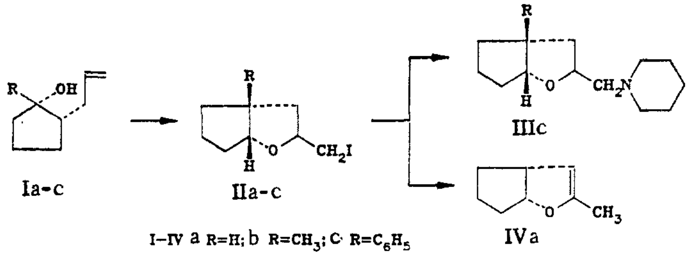
Derivatives of cyclopenta[b]tetrahydrofurans are formed as a result of the iodocyclization of cis-1-R-2-allylcyclopentan-1-ols. The iodocyclization reaction of unsaturated alcohols is described by a kinetic equation of the second order (the first order for each of the reagents).

It was shown [1] that the iodination of cis- and trans-1-R-2-allylcyclohexan-1-ols proceeds with the formation of the mixture of the stereoisomeric octahydrobenzofurans. The rates of the iodination of the cis- and trans-isomers are approximately the same.

With the object of investigating the influence of the structure of the cyclic alcohols on their reactivity in the electrophilic heterocyclization reactions, we studied the iodocyclization of the 1-R-2-allylcyclopentan-1-ols (Ia-c). The investigation of the stoichiometry of the iodination showed that the consumption of the iodine in the reaction corresponds to the percentage content of the cis-isomer in the alcohols (IIa-c) were obtained as a result of the iodination of the compounds (Ia-c) in an aqueous solution of KI.



I–IV a R=H; b $R=CH_3$; C $R=C_6H_5$

The interpretation of the PMR spectra of the furans (IIa-c) was hampered due to their complexity. The structure of the compounds was demonstrated using the IR spectra, the elemental analysis, and literature analogies [2]. Since the furan (IIc) is thermally unstable, its derivative (IIIc) was obtained by the reaction with piperidine in benzene; the treatment of compound (IIa) with alkali in ether gives the known furan (IVa) [3].

Therefore, in contrast to the 2-allylcyclohexanols, for which both the cis- and the trans-isomers undergo the iodocyclization [1], only the cis-isomers enter into the reaction in the case of the compounds (Ia-c); this is determined by the relative configurational rigidity of the cyclopentane ring. This fact raises the possibility of utilizing the iodocyclization reaction for the iodometric determination of the cis-isomers in the mixture of the cis- and trans-isomers of the alcohols (Ia, b), as well as for the synthesis of prostacyclins and homoprostacyclins [2, 4].

The kinetics of the iodocyclization of the compounds (Ia-c) were studied by the method of [5] using the phosphate buffer (0.2 M) in the pH range of 6.8-7.5 with the $1-8\cdot10^{-3}$ M concentrations of the alcohols (Ia-c) and iodine and the 0.06-0.5 M concentrations of KI at the temperatures of 20-40°C. It was established that the iodocyclization reaction of the 2-allylcyclopentanols is described by the kinetic equation

$$-d[I_2]/dt=k_2[UA][I_2],$$

where [UA] is the analytical concentration of the cis-isomer of the unsaturated alcohol, and $[I_2]$ is the concentration of the molecular iodine which is not bound in the complex I_3^-.

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TABLE 1. Kinetic and Activation Parameters of the Iodocyclization of the cis-1-R-2-Allylcyclopentanols (Ia-c) and the cis-1-R-2-Allylcyclohexanols (Va-c) [1]

Compound	R	k at 20°C, dm^3/(mole·sec)	$E^{\neq}$, kJ/mole	$-\Delta S^{\neq}$, J/(mole·K)	log A
Ia	H	28,5±1,4	42,3±0,7	81.0±5,2	37,7±1,5
Ib	CH_3	21,6±1,1	47,7±3,2	65,1±4,3	41,1±1,1
Ic	C_6H_5	3,9±0.2	50,5±2.1	69.2±3,2	40,3±1,1
Va	H	27,5±1,5	49,7±2,1	54.8±7,1	38,6±1,6
Vb	CH_3	67,0±2,0	45,1±2,5	63.5±8,4	35,5±1,9
Vc	C_6H_5	2,3±0,2	38,0±1,0	116,3±3,5	29,5±1,1

The values of the rate constants of the iodocyclization of the alcohols (Ia-c) at 20°C and the thermodynamic characteristics of the reaction are presented in Table 1. It can be seen from Table 1 that the rates of the iodocyclization of the compounds (Ia-c) and the 2-allylcyclohexanols (Va-c) [1] are comparable. The insignificant differences in the rates may be related to the nature of the cyclopentane and cyclohexane rings. A decrease in the rate of the iodocyclization of the alcohol (Ic) is observed as in the case of the iodination of cis-2-allyl-1-phenylcyclohexanol; this is evidently associated with the steric influence of the bulky phenyl group.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer. The purity and isomeric composition of the initial alcohols were determined on a Tsvet-4 chromatograph with a catharometer detector. The column of 3000 × 3 mm had the sorbent of 10% Tween-80 on Chromaton N-AW-DMCS (0.25-0.315 mm). The temperature of the vaporizer was 250°C; the temperature of the column was 140-180°C. The gas carrier was nitrogen; the flow rate was 60 ml/min. The isomeric composition of the alcohols was confirmed by the study of the stoichiometry of the iodination reaction.

2-Allylcyclopentanol (Ia). This compound (30% cis- and 70% trans-) was obtained by the reaction of 10 g (0.08 mole) of 2-allylcyclopentanone with 4.5 g (0.12 mole) of $LiAlH_4$ in abs. ether. The mixture is stirred for 2 h at 20°C, and the excess of the $LiAlH_4$ is decomposed with ice water. The ether layer is separated, dried with magnesium sulfate, and distilled. The bp is 44-46°C (2 mm of Hg stem). The n_D^{20} is 1.4694, and the d_4^{20} is 0.9186. The IR spectrum is as follows: 1640 (C=C) and 3350 cm^{-1} (OH).

1-Methyl-2-allylcyclopentanol (Ib). This compound (65% cis- and 35% trans-) was obtained by the dropwise addition of 7.0 g (0.056 mole) of 2-allylcyclopentanone to methylmagnesium iodide, obtained from 7.9 g (0.056 mole) of methyl iodide and 1.37 g (0.056 mole) of metallic magnesium in abs. ether. The mixture was stirred for 2 h at 20°C prior to the decomposition with a saturated solution of NH_4Cl. The ether layer was separated, and the aqueous layer was extracted with ether (2 portions of 150 ml). The combined ether extracts were dried with $MgSO_4$. The ether was evaporated, and the residue was distilled. The yield was 50%. The product has the bp 52-54°C (2 mm of Hg stem), the n_D^{23} 1.4680, and d_4^{23} 0.9163. Found, %: C 77.2; H 11.6. MR_D 42.5. $C_9H_{16}O$. Calculated, %: C 77.1; H 11.5. MR_D 42.6. The IR spectrum is as follows: 1645 (C=C) and 3370 cm^{-1} (OH).

cis-1-Phenyl-2-allylcyclopentanol (Ic). This compound was obtained analogously to the alcohol (Ib) from 6.0 g (0.048 mole) of 2-allylcyclopentanone, 7.6 g (0.048 mole) of bromobenzene, and 1.17 g (0.048 mole) of magnesium. The yield was 53%. The product has the bp 115-118°C (2 mm of Hg stem), the n_D^{23} 1.5442, and the d_4^{23} 1.0165. Found, %: C 83.2; H 8.9. MR_D 62.4. $C_{14}H_{18}O$. Calculated, %: C 83.1; H 9.0. MR_D 62.2. The IR spectrum is as follows: 1650 (C=C), 1600 (C_6H_5) and 3350 cm^{-1} (OH).

The iodination of the alcohols (Ia-c) was carried out by the method described in the work [6].

2-(Iodomethyl)cyclopenta[b]tetrahydrofuran (IIa). This compound was obtained by the iodination of the alcohol (Ia). The yield was 85%. The product has the bp 90-92°C (2 mm of Hg stem) and the n_D^{22} 1.5495. Found, %: C 38.1; H 5.1; I 50.3. $C_8H_{13}IO$. Calculated, %: C 38.1; H 5.3; I 49.9. The IR spectrum is characterized at 1090 cm^{-1} (C–O–C). The treatment of 2.5 g (0.01 mole) of the compound (IIa) with powdered NaOH (0.02 mole) in abs. ether leads to the isolation of 2-methylcyclopenta[b]dihydrofuran (IVa) which is completely identical with the product obtained by the mercury-cyclization of 2-propargylcyclopentanol [3].

2-(Iodomethyl)-6a-methylcyclopenta[b]tetrahydrofuran (IIb). This compound was obtained by the iodination of the alcohol (Ib). The yield was 87%. The product has the bp 96-98°C (2 mm of Hg stem) and the n_D^{20} 1.5308. Found, %: C 40.9; H 5.4; I 48.0. $C_9H_{15}IO$. Calculated, %: C 40.6; H 5.7; I 47.7. The IR spectrum is characterized at 1095 cm^{-1} (C–O–C).

2-(Piperidinomethyl)-6a-phenylcyclopenta[b]tetrahydrofuran (IIIc). This compound was obtained by the iodination of 3.0 g (0.015 mole) of the alcohol (Ic) and the subsequent treatment of the furan (IIc) with the solution of 2.56 g (0.03 mole) of piperidine in benzene for 3 h at 80°C. The mixture is cooled, and the precipitated piperidine hydriodide salt is filtered off prior to the evaporation of the filtrate and distillation. The yield of the compound (IIIc) was 75%. The product has the bp 140-142°C (2 mm of Hg stem) and the n_D^{23} 1.5389. Found, %: C 79.8; H 9.3; N 5.1. $C_{19}H_{27}NO$. Calculated, %: C 80.0; H 9.5; N 4.9.

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ELECTRON STRUCTURES AND ^{13}C NMR SPECTRA OF 3-SUBSTITUTED COUMARIN DERIVATIVES

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Quantum-chemical calculation of the electron densities on the atoms and the Wiberg indexes in coumarin and 3-amino-3-hydroxy-, and 3-carboxycoumarin molecules within the CNDO/2 approximation was accomplished. The ^{13}C NMR spectra of the indicated compounds were recorded. The effect of the nature of the substituent in the pyrone ring on the electron structures of 3-substituted coumarin derivatives was evaluated on the basis of the data obtained. The character and degree of the relationship between the chemical shifts and the electron densities on the carbon atoms were established by means of regression analysis.

Coumarins are included among natural organic compounds that have diverse biological activity [1].

The chemical properties of coumarins have been studied rather fully [1, 2]. Attempts have been made to provide a basis for the reactivities of a number of coumarin derivatives from the results of quantum-chemical calculations by the Hückel [3] and Pariser–Parr–Pople (PPP) methods [4]. Some correlations between the calculated reactivity indexes and the

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