STUDY OF FORMATION MECHANISM OF 1,3-BENZODIOXANES FROM TERTIARY PHENOLOALCOHOLS AND CARBONYL COMPOUNDS USING LABELED ATOMS

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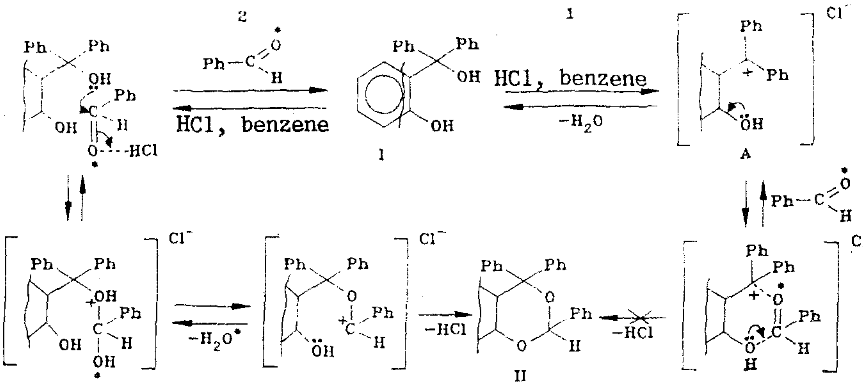
UDC 547.841'631.20.4:541.124

It was shown that the reaction of o-hyroxyphenyldiphenylmethanol with benzaldehyde labeled with ^{17}O and ^{18}O isotopes proceeds in such a way that oxygen atoms of the starting phenoloalcohol are retained.

The present work is a continuation of the investigation of the formation process of a six-membered heterocyclic ring annelated with the benzene ring [1-3]. The object of these investigations are 2,4-substituted 1,3-benzodioxanes formed during the condensation of tertiary phenoloalcohols with carbonyl compounds [4]. According to present concepts, this closure of the hetero ring [2, 3] can be accomplished by two paths: by an electrophilic addition of a benzyl-type carbocation formed, from the phenoloalcohols in an acid medium, to the oxygen atom of the carbonyl compound (path 1), or via an initial nucleophilic addition of the oxygen atom of the tertiary alcoholic group to the carbon atom of the carbonyl group (path 2).



The formation of the 1,3-benzodioxanes was studied using as an example the reaction of o-hydroxyphenyldiphenylmethanol (I) with benzaldehyde enriched by ^{17}O and ^{18}O isotopes. The analysis of the starting compounds and the products was carried out by ^{17}O NMR spectroscopy and mass spectrometry. According to the analysis results, the enrichment of the initial aldehyde by the ^{17}O isotope is 7.6% and with the ^{18}O isotope 48%.

The method of preparation of 2,4,4-triphenyl-1,3-benzodioxane II consisted in boiling the starting reagents in absolute benzene with azeotropic distillation of the water formed. As the starting catalyst we used dry gaseous HCl, with which the reaction mixture was saturated before the beginning of the reaction. The mixture thus acquired a red-pink color, which disappeared when heating commenced. This phenomenon of halochromy may indicate the presence of a conjugated cation A in the solution.

The 1,3-benzodioxane II obtained did not give a signal in the ^{17}O NMR spectrum, while the spectrum of the water that separated out indicated the presence of the ^{17}O isotope in an amount of 0.425% (at its natural content of 0.0397%). These data provide convincing arguments for the retention of the oxygen atoms of the hydroxyl groups of the initial phenoloalcohol in the reaction product — 1,3-benzodioxane II during the process (path 2).

Direct examination of 1,3-benzodioxane II for the content of the isotopic tracer by mass spectrometry was impossible: the molecular ion was absent in its spectrum. Therefore the water separating out during the reaction was subjected to isotopic exchange [5] with an unlabeled benzaldehyde (III) according to the equation:

$$H_2O^* + \underset{III}{C_6H_5{-}CHO} \overset{H^+}{\rightleftharpoons} H_2O + \underset{III^*}{C_6H_5{-}CHO^*}$$

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0009-3122/91/2705-0502$12.50

The mass spectrometric examination of the enriched benzaldehyde (III*) revealed a 9% content of the ^{18}O isotope in it, which serves as still another proof for the acetalation mechanism (path 2), at which the oxygen atom of the oxo group is included in the composition of the water molecule, and not in the heterocyclic compound formed. Here, as in the case of formation of 1,2-dihydro-4H-3,1-benzoxazines [3], cation A does not participate in the closure of the heterocyclic ring.

EXPERIMENTAL

The ^{17}O NMR spectra were obtained on a Bruker WP-200 SY spectrometer in a pulse regime with a Fourier transformation. The sample of 1,3-benzodioxane II was in the form of a saturated solution of the preparation in absolute chloroform. The recording conditions of the spectra were as follows: working frequency for the ^{17}O nucleus 27.13 MHz; scanning width 50 kHz, pulse duration 50 μsec, lag between pulses 300 μsec. Number of pulses during recording of the benzaldehyde spectrum 10,000, for nonenriched and enriched water — 1000, and for the remaining substrates — 842,000. The mass spectra were recorded on an MX-1320 mass spectrometer at an ionizing electron energy of ~12 eV.

o-Hydroxyophenyldiphenylmethanol (I) was obtained by the reaction of methyl salicylate with phenylmagnesium bromide according to a known method [6].

2,4,4-Triphenyl-1,3-benzodioxane (II). A 2.76 g portion (10 mmoles) of phenoloalcohol I, 10.05 g (10 mmoles) of benzaldehyde enriched with ^{17}O and ^{18}O isotopes and 20-25 ml of absolute benzene were placed in a 50 ml flat-bottomed flask equipped with a magnetic stirrer, a Dean—Stark adapter, and reflux condenser with a calcium chloride tube. Dry gaseous HCl was passed through this mixture in the cold for 20 min. The mixture was then heated with stirring to the boiling point and was boiled to a complete separation of the calculated amount of water in the Dean—Stark adapter. After evaporation of the solvent, the residue was crystallized from petroleum ether. The yield of benzodioxane II was 3.4 g (85%). Its physical constants corresponded to the published data [4].

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