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MECHANISM OF REACTION OF PHENYL GLYCIDYL ETHER WITH PHENYL BENZOATE IN THE PRESENCE OF WATER

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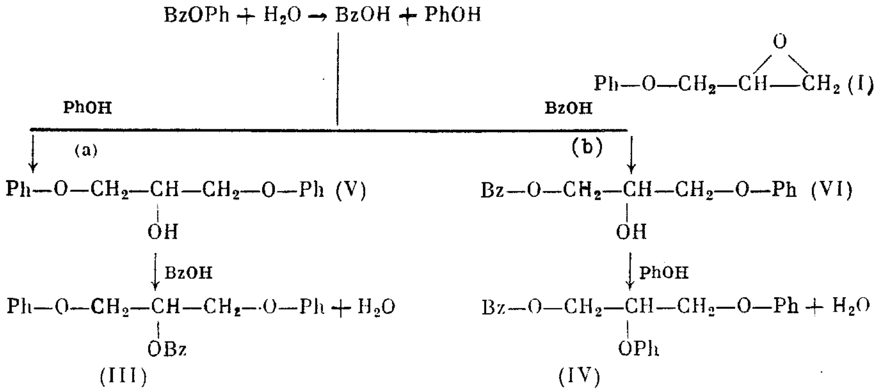
UDC 541.124:542.91:547.474.
3'562:547.581.2'562

The reaction of phenyl glycidyl ether with phenyl benzoate in the presence of water was investigated by adsorption liquid chromatography.

One of the novel reactions of α-oxy compounds that are now being widely studied is their reaction with ester groups [1]. This reaction is finding greater and greater use in the preparation of novel heterochain polymers [2] and also for crosslinking of polyesters [3, 4]. As a result of the reaction, normal cleavage of the α-oxy ring occurs (at the CH_2–O bond) with its subsequent addition at the ester bond. Thus, it has been shown [3, 5] that the reaction of phenyl glycidyl ether (I) with BzOPh (II) affords 1,3-diphenyl-2-benzoylglycerol (III).

In a number of cases [6, 7], the occurrence of polymer-degradation processes due to hydrolysis of ester bonds by sorption moisture has been noted in the reaction of epoxy oligomers with aromatic polyesters (polyarylates) under severe conditions (180°C for 10 h). With model compounds, it has been shown [3] that the reaction of phenyl benzoate (II) with glycerol α-phenyl ether, a product of the hydrolysis of phenyl glycidyl ether (I), does not afford addition product (III) or 1,2-diphenyl-3-benzoylglycerol (IV).

However, another route of the reaction involving water which affords product (III) or (IV) during normal cleavage of the α-oxy ring of phenyl glycidyl ether is possible:



But in the case of anomalous cleavage of the α-oxy ring (at the CH–O bond), the occurrence of the reaction by route (a) in the proposed scheme should afford (IV), and its occurrence by route (b) should afford (III). In addition, in both cases, there is no event of direct addition of an α-oxy ring at the ester bond of phenyl benzoate.

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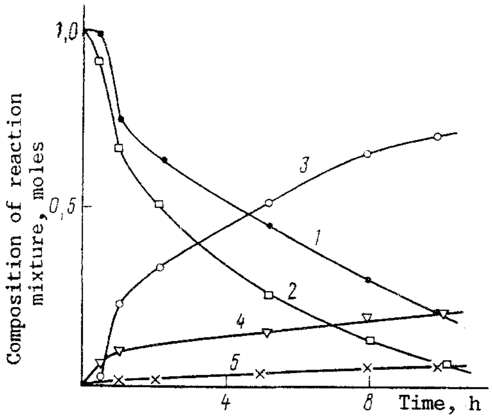

Fig. 1. Change of the composition and products of the reaction of phenyl benzoate, phenyl glycidyl ether, and water in relation to the reaction time at 200 °C in the presence of 0.05 mole of sodium benzoate: 1) (I); 2) (II); 3) (III); 4) phenol; 5) (V) + (IV).

The purpose of the present paper is an investigation of the effect of hydrolysis of the ester bond on the occurrence of the reaction of aromatic esters with α-oxy compounds.

DISCUSSION OF RESULTS

The reaction of phenyl glycidyl ether with phenyl benzoate (1:1, mole) in the presence of 0.3 mole of water and 0.05 mole of BzONa as a catalyst was carried out in a melt at 200°C.

An analysis of the reaction material (Fig. 1) showed that the main product of the reaction is (III). Compound (IV) was not formed under the investigated conditions. At the same time, the ester bond of BzOPh is hydrolyzed during the main reaction: up to 0.2 mole fraction of PhOH and also insignificant amounts of products of the addition of PhOH and BzOH to phenyl glycidyl ether (V) and (VI) were observed in the reaction products.

To investigate the possibility of occurrence of the reaction according to the proposed scheme, we carried out the reaction of PhOH, BzOH, and phenyl glycidyl ether in a 1:1:2 mole ratio, respectively.

Chromatographic analysis of the reaction material showed that after 15 min of thermostating of the system practically quantitative addition of BzOH to (I) occurred with the formation of product (VI). At the same time, we observed slower formation of 1,3-diphenylglycerol (V) as a result of addition of phenol to (I). After completion of the reaction, practically quantitative conversion of (I) had been attained, with the reaction products consisting of a mixture of oligomeric compounds that were formed as a result of the reaction of (I) with secondary alcohols (V) and (VI). Under the investigated conditions, we observed no formation of (III) or (IV) even until complete consumption of the starting components.

Thus, from the obtained results, we can conclude that the hydrolysis of the aromatic ester bond is a side reaction that occurs parallel to the reaction of addition of the α-oxy ring at the ester bond when water is present in the system. This affords phenol and carboxyl groups which, during reaction with α-oxy compounds, form products containing secondary hydroxyl groups. These processes occur separately from the main addition reaction, and their rate is limited by the amount of sorption moisture contained in the system.

EXPERIMENTAL

The reaction of 1 mole of phenyl glycidyl ether with 1 mole of BzOPh in the presence of 0.3 mole of water and 0.05 mole of BzONa was carried out in a melt at 200°C. The composition of the reaction material during the reaction was analyzed by adsorption liquid chromatography [8].

Phenyl glycidyl ether (I) was purified by distillation, bp 79-81°C (1 mm) [9]. Phenyl benzoate (II) was obtained according to [10], mp 67.5-68.5°C (hexane). 1,3-Diphenylglycerol (V) was obtained by the reaction of phenyl glycidyl ether with phenol, bp 190-191°C, mp 80-81°C (hexane) [11]. 1,3-Diphenyl-2-benzoylglycerol (III) was obtained by condensation of 1,3-diphenylglycerol with BzCl in the presence of NEt_3, mp 67-68°C (hexane) [5].

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SYNTHESIS AND CERTAIN PROPERTIES OF ACETYLENYLINDOLES

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UDC 542.953:547.754:547.
538.241:541.69

A group of new acetylenic derivatives of indole was synthesized by condensation of 2- and 3-iodoindoles with terminal acetylenes. 3-Iodoindole unsubstituted at the heteroatom is distinguished by an increased tendency to undergo deiodination under the reaction conditions. Chemical transformations of the synthesized acetylenic derivatives were carried out, proceeding with both the retention of and with the participation of the triple bond. In the intramolecular cyclization of vicinal, functionally substituted indolylacetylenes, a tendency is manifested to form six-membered heterocycles. A primary pharmacological investigation of the compounds obtained was carried out. Most of them are slightly toxic, several of the compounds display in high doses indications of neurotropic activity.

Many natural and synthetic compounds of the indole series find application as effective medicinal preparations [1]. Because of the high reactivity of the acetylenic grouping, acetylenylindoles are promising intermediates in the synthesis of various indole derivatives, including biologically active compounds. It is probable that indolylacetylenes may also possess direct biological activity (see, for example, [2]). Therefore, in the present work, new acetylenic derivatives of indole were prepared, their chemical transformations were performed, and primary biological tests were carried out.

Acetylenylindoles were obtained by condensation of iodoindoles with terminal acetylenes in the presence of $Pd[PPh_3]_2Cl_2$—CuI or with copper acetylenides [3-5].

The catalytic condensation of 3-iodoindoles unsubstituted at the nitrogen atom, as in the case of the analogous 3-iodopyrroles [6], was accompanied, and in many cases was also suppressed, by the competing reaction of reductive dehalogenation. Thus, iodide (Ia) when heated with phenylacetylene (II) and a catalyst in pyridine in the presence of K_2CO_3, and iodoacetylenylindole (Ib) – with 2-methylbutyn-3-ol (III) in Et_2NH, were converted into deiodination products (IVa, b) in a 80-90% yield

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