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LETTERS TO THE EDITOR

RECYCLIZATION IN THE HYDRATION OF 3-FORMYL-2-PHENYL-1,4-BENZODIOXINE

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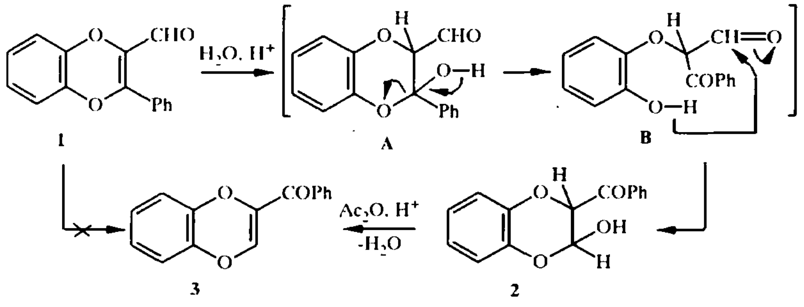
2-Ethyl-3-formylbenzo[*b*]furan recyclizes upon treatment with hydrochloric acid to an isomeric ketone, namely, 3-propionylbenzo[*b*]furan [1].

The conversion of 2-phenyl-3-formyl-1,4-benzodioxine (**1**) proceeds as follows. The action of hydrochloric acid leads to the addition of water at the double bond in the non-aromatic heterocycle. Resultant hemiketal **A** is unstable and recyclizes under the reaction conditions. Ordinary ring–chain tautomeric conversion probably occurs to give the also unstable non-heterocyclic hydroxydicarbonyl species **B**, in which the intramolecular addition of the hydroxyl group proceeds at the more reactive formyl carbonyl group. A stable heterocyclic hemiacetal **2** is formed. The lack of a signal for an aldehydic proton in the ^{1}H NMR spectrum supports the assigned structure. Dehydration to ketone **3**, which is isomeric to starting aldehyde **1**, does not proceed spontaneously but rather upon treatment with acetic anhydride using sulfuric acid as the catalyst.



These transformations are preparatively convenient. Products **1-3** are new 1,3-dielectrophiles, in which one of the reaction sites is in the heterocycle. Such compounds [2] may react with dinucleophiles with opening of the starting ring and are irreplaceable in the synthesis of many functionalized heterocycles.

3-Formyl-2-phenyl-1,4-benzodioxine (1) was obtained in the Vilsmeier reaction using DMF (4.6 ml, 60 mmol), $POCl_3$ (1.1 ml, 12 mmol), and 2-phenyl-1,4-benzodioxine (2.1 g, 10 mmol) (obtained according to our previous procedure [3]) at 20°C over 24 h. The mixture was treated with a solution of 6.12 g sodium acetate trihydrate in 7 ml water and heated with stirring until the onset of crystallization. After cooling, the precipitate was filtered off and washed with water and 2-propanol to give 2.27 g (95%) of compound **1**; mp 106-107°C (2-propanol). IR spectrum: 1625 (C=C); 1654 cm^{-1} (C=O). ^{1}H NMR spectrum (300 MHz, acetone-d_6): 6.89-7.04 (4H, m, C_6H_4); 7.57-7.74 (5H, m, C_6H_5); 9.2 ppm (1H, s, CH=O). Found, %: C 75.85; H 4.31. $C_{15}H_{10}O_3$. Calculated, %: C 75.62; H 4.23.

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3-Benzoyl-2,3-dihydro-1,4-benzo-2-dioxinol (2). A mixture of compound **1** (1.19 g, 5 mmol) and acetic acid (2 ml) was heated until homogeneous. Then, a solution of concentrated hydrochloric acid (0.1 ml) in water (1 ml) was added. The mixture was heated until the onset of product crystallization and then maintained at 95-100°C for 45 min. After cooling, the precipitate was filtered off and washed with 1:1 water–2-propanol. Yield 1.21 g (94%); mp 171-174°C (acetic acid). IR spectrum: 1680 (C=O); 3420 cm^{-1} (O–H). ^{1}H NMR spectrum (300 MHz, DMSO-d$_6$): 5.65 (1H, d, *J* = 6.9 Hz, CHC=O); 5.79 (1H, s, OH); 6.82-6.98 (4H, m, C_6H_4); 7.53-8.02 (6H, m, C_6H_5 + OCHO). Found, %: C 70.21; H 4.63. $C_{15}H_{12}O_4$. Calculated, %: C 70.30; H 4.72.

2-Benzoyl-1,4-benzodioxine (3). A mixture of compound **2** (2.08 g, 8.1 mmol), acetic anhydride (6 ml), and one drop of concentrated sulfuric acid was stirred for 15 min. Then, potassium acetate (0.82 g, 8.4 mmol) was added and the mixture was heated at reflux with stirring for 2 min. After cooling, a mixture of water (6 ml) and 25% aqueous ammonia (6 ml) was added with stirring and cooling with running water. The precipitate was filtered off and washed with 1:1 water–2-propanol to give 1.93 g (100%) of compound **3**; mp 80-81°C (2-propanol). IR spectrum: 1620 (C=C); 1640 cm^{-1} (C=O). ^{1}H NMR spectrum (300 MHz, acetone-d$_6$): 6.83-7.05 (4H, m, C_6H_4); 7.02 (1H, s, OCH); 7.50-7.81 ppm (5H, m, C_6H_5). Found, %: C 75.55; H 4.29. $C_{15}H_{10}O_3$. Calculated, %: C 75.62; H 4.23.

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