LETTERS TO THE EDITOR

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

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2-Ethyl-3-formylbenzo[*b*]furan when treated with hydrochloric acid undergoes recyclization to form the isomeric ketone: 3-propionylbenzo[*b*]furan [1].

Here we are reporting on the specific conversion of 3-formyl-2-phenyl-1,4-benzodioxin (I). When it is treated with hydrochloric acid, addition of water occurs at the multiple bond of the non-aromatic heterocycle. The polyketal A formed is unstable, and under the reaction conditions it undergoes recyclization. Probably the usual ring-chain tautomeric conversion occurs up to the also unstable open form B, in which intramolecular addition of the hydroxyl group proceeds at the more reactive formyl carbonyl. So the stable heterocyclic polyacetal II is formed. The absence of a signal from the aldehyde proton in the PMR spectrum confirms the structure of the compound. Dehydration to ketone III (isomeric to the starting aldehyde I) does not occur spontaneously but rather when it is treated with acetic anhydride in the presence of sulfuric acid as a catalyst.



The conversions under discussion are convenient for preparative syntheses. Compounds I-III are novel 1,3-dielectrophiles in which one of the reaction centers is located on the heterocycle. Compounds of this type can react with dinucleophiles with opening of the original ring, and are indispensable in syntheses of many functionalized heterocycles [2].

3-Formyl-2-phenyl-1,4-benzodioxin (I). The product was obtained by treatment (20°C, 24 h) of 2-phenyl-1,4-benzodioxin (2.1 g, 10 mmol) (obtained by the method [3]) with DMF (4.6 ml, 60 mmol) and phosphorus oxychloride (1.1 ml, 12 mmol). The mixture was treated with a solution of AcONa·3H₂O (6.12 g) in water (7 ml) and heated with stirring until crystallization began. After cooing down, the precipitate was filtered off and then washed with water and 2-propanol. Yield 2.27 g (95%); mp 106-107°C (2-propanol). PMR spectrum (300 MHz, acetone-d₆): 6.89-7.04 (4H, m, C₆H₄); 7.57-7.74 (5H, m, C₆H₅); 9.22 (1H, s, CH=O). IR spectrum: 1625 (C=C), 1645 cm⁻¹ (C=O). Found, %: C 75.85; H 4.31. C₁₅H₁₀O₃. Calculated, %: C 75.62; H 4.23.

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0009-3122/99/3512-1480\$22.00©1999 KluwerAcademic/Plenum Publishers

3-Benzoyl-2,3-dihydro-1,4-benzodioxin-2-ol (II). A mixture of compound I (1.19 g, 5 mmol) and acetic acid (2 ml) was heated to homogenization, then a solution of concentrated hydrochloric acid (0.1 ml) in water (1 ml) was added. This was boiled until crystallization of the product began, and then it was allowed to stand for 45 min at 95-100°C. After cooling, the precipitate was filtered off and then washed with aqueous 2-propanol (1:1). Yield 1.21 g (94%); mp 171-174°C (acetic acid). PMR spectrum (300 MHz, DMSO-d₆): 5.65 (1H, d, CHC=O, J = 6.9 Hz); 5.79 (1H, s, OH); 6.82-6.98 (4H, m, C₆H₄); 7.53-8.02 (6H, m, C₆H₅ + OCHO). IR spectrum: 1680 (C=O), 3420 cm⁻¹ (OH). Found, %: C 70.21; H 4.63. C₁₅H₁₂O₄. Calculated, %: C 70.30; H 4.72.

2-Benzoyl-1,4-benzodioxin (III). A mixture of compound II (2.08 g, 8.1 mmol), acetic anhydride (6 ml), and 1 drop of concentrated sulfuric acid was stirred for 15 min. Potassium acetate (0.82 g, 8.4 mmol) was added and this mixture was boiled with stirring for 2 min. After cooling, a mixture of 6 ml water and 6 ml 25% aqueous ammonia was added with stirring and cooling under running water. The precipitate was filtered off and then washed with water and aqueous 2-propanol (1:1). Yield 1.93 g (100%); mp 80-81°C (2-propanol). PMR spectrum (300 MHz, acetone-d₆): 6.83-7.05 (4H, m, C₆H₄); 7.02 (1H, s, OCH); 7.50-7.81 (5H, m, C₆H₅). IR spectrum: 1620 (C=C), 1640 cm⁻¹ (C=O). Found, %: C 75.55; H 4.29. C₁₅H₁₀O₃. Calculated, %: C 75.62; H 4.23.

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