Dehydration of 2,2'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl under bromine action as a new way to prepare dibenzofuran derivatives

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We found that the action of bromine on 2,2'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (**1**) in glacial CH_3COOH results in an almost immediate quantitative formation of 2,4,6,8-tetra-*tert*-butyldibenzofuran (**2**). Bisphenol **1** is stable in CH_3COOH and $CH_3COOH-HBr$; therefore, the key role in the observed anhydroheterocyclization is evidently played by Br_2, which likely acts as an electrophilic catalyst. It is reasonable to suppose that the mechanism of the catalytic process involves the formation of complex **1** with Br_2 (**3**), whose structure corresponds to that of the σ-complex of aromatic substitution, in which the positive charge and spatial closeness of the hydroxyl groups favor dehydration, and the regeneration of the aromatic structure in the absence of the mobile proton in a new σ-complex (**4**) is followed by the loss of Br^+, *i.e.*, regeneration of Br_2. This mechanism of "phantom bromination" for the formation of compound **2** also explains the effect of addition of H_2O, which partially suppresses dehydration and directs the transformation of complex **3** *via* the parallel route resulting in the formation of bromoquinolide compounds **5** and **6**.

Compounds **2**, **5**, and **6** were isolated preparatively. The data on 2,4,6,8-tetra-*tert*-butyldibenzofuran (**2**), m.p. 208—209 °C (from CH_3OH), correspond to the literature data.[1] The data on bis-(5-bromo-3,5-di-*tert*-butylcyclohexadien-3,6-one-2) (**5**), m.p. 137—138 °C (from ether), and 4-bromo-1-oxo-2,4,6,8-tetra-*tert*-butyldihydrodibenzofuran (**6**), m.p. 182—183 °C (from ether), correspond to the data of Ref. 2.

Analysis of the literature data[3,4] shows that the Br_2-catalyzed transformation of compound **1** to compound **2** is one of the simplest ways of preparation of dibenzofuran and its derivatives.

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