SYNTHESIS OF DIBENZOFURAN DERIVATIVES*

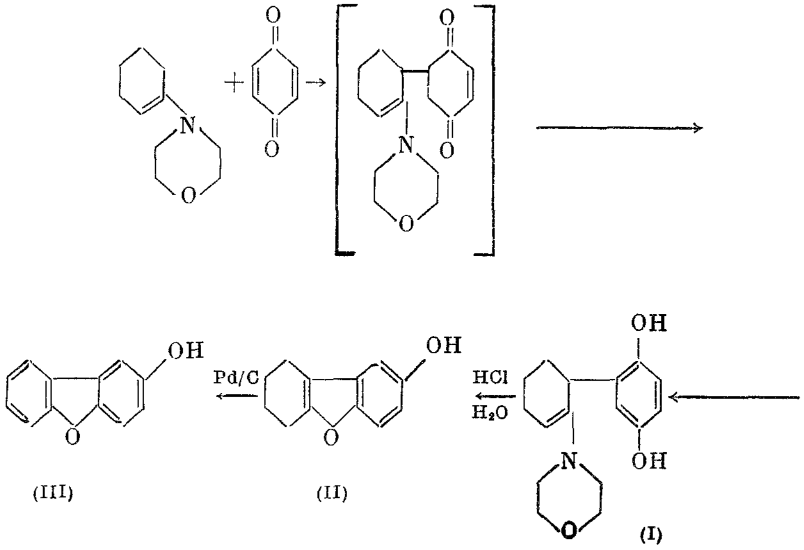
(UDC 542.91)

S. I. Zavyalov, G. V. Kondrat'eva, and V. I. Gunar

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11,
pp. 2086-2087, November, 1964
Original article submitted March 25, 1964

In the reaction of p-benzoquinone with 1-morpholinocyclohexene-1 in benzene, 1-morpholino-6-(2',5'-dihydroxyphenyl)cyclohexene-1 (I) is formed; under the influence of hydrochloric acid, it undergoes hydrolysis, with simultaneous cyclization to 2-hydroxy-6,7,8,9-tetrahydrodibenzofuran (II)



The unconjugated position of the double bond in the molecule of the adduct (I), as more energetically profitable, was assumed by analogy with other substituted cyclic enamines [1], while the structure of the hydrolysis product (II) was confirmed by its dehydrogenation over palladium-coated charcoal to the known 2-hydroxydibenzofuran (III) [2].

EXPERIMENTAL

1-Morpholino-6-(2',5'-dihydroxyphenyl)cyclohexene-1 (I). To a solution of 1 g of p-benzoquinone in 10 ml of benzene at 20° we added 2 g of 1-morpholinocyclohexene-1 [1]. The reaction was accompanied by a substantial thermal effect, and the temperature of the solution rose to 60-65°. After 1 h of standing at −20° and cooling with ice water, the precipitate that formed was filtered off and washed with benzene. We obtained 2.5 g (72%) of 1-morpholino-6-(2',5'-dihydroxyphenyl)cyclohexene-1 (I), solvated with benzene, m.p. 90-92°; λ_{max} 218, 231, 304 mμ (ε 4450, 4250, 3910) (here and henceforth in alcohol). Found: N 3.93, 3.96%. $C_{16}H_{21}O_3N \cdot C_6H_6$. Calculated: N 3.98%.

A 3-g portion of the solvate described above was heated at 140-150° until complete distillation of the benzene (10-15 min). After cooling, the solid residue was washed with ether, and we obtained 2 g of 1-morpholino-6-(2',5'-dihydroxyphenyl)cyclohexene-1 with m.p. 145-150°. After recrystallization from a mixture of heptane and ethyl

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*During the preparation of this work for print, this method of synthesis was published by Domschke [G. Domschke, Z. Chem., 4 (I), 26 (1964)] in the form of a Brief Communication, without experimental section.

acetate, m.p. 150-152°; λ_{max} 218, 232, 304 mμ (ε 3760, 3960, 4220). Found: N 5.45%, 5.49%. $C_{16}H_{21}O_3N$. Calculated: N 5.09%.

2-Hydroxy-6,7,8,9-tetrahydrodibenzofuran (II). A mixture of 1 g of the solvate of 1-morpholino-6-(2',5'-dihydroxyphenyl)cyclohexene-1 and 10 ml dilute hydrochloric acid (1:1) was heated to boiling, and extracted with ether upon cooling. After evaporation of the extract, we isolated 0.5 g (93%) of 2-hydroxy-6,7,8,9-tetrahydrodibenzofuran (II), with m.p. 100-102°. After recrystallization from benzene, m.p. 102-103°, b.p. 176-178° (3 mm); λ_{max} 256, 295 mμ (ε 8560, 3330). Found: C 76.30, 76.36; H 6.20, 6.29%. $C_{12}H_{12}O_2$. Calculated: C 76.57; H 6.43%.

2-Hydroxydibenzofuran (III). A mixture of 0.5 g of 2-hydroxy-6,7,8,9-tetrahydrodibenzofuran and 0.5 g of 10% palladium on charcoal was heated at 310-320° until the evolution of hydrogen ceased (20-30 min) and then treated with 5% alkali. Upon acidification of the filtered solution with concentrated hydrochloric acid, 0.25 g (53%) of 2-hydroxydibenzofuran (III) with m.p. 125-127° precipitated. After recrystallization from toluene, m.p. 132-133°. The substance obtained gave no depression of the melting point in a mixed melting point test with a known sample (m.p. 134-135°) [2].

In conclusion, let us express our gratitude to G. A. Kogan for taking the ultraviolet spectra.

SUMMARY

In the reaction of p-benzoquinone with 1-morpholinocyclohexene-1 and subsequent acid hydrolysis of the addition product, 2-hydroxy-6,7,8,9-tetrahydrodibenzofuran is formed, in a total yield of 67%.

LITERATURE CITED

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2. K. Schimmelschmidt, Liebigs Ann. Chem., 566, 184 (1950).