Formation of 3,3´,5,5´-tetra(*tert*-butyl)diphenoquinone and 3,3´,5,5´-tetra(*tert*-butyl)-4,4´-dihydroxybiphenyl in the reaction of 2-(acetylamino)-3-[3´,5´-di(*tert*-butyl)-4´-hydroxyphenyl]propanoic acid with thionyl chloride

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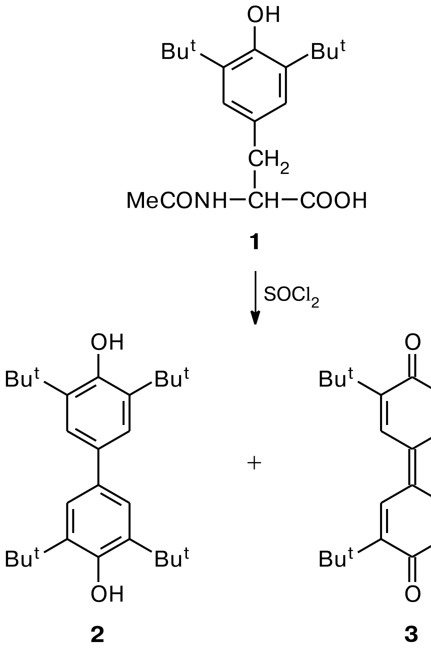
Thionyl chloride is a reagent, which reacts with amino acid acetyl derivatives to yield corresponding acyl chlorides. However, a reaction of 2-(acetylamino)-3-[3´,5´-di(*tert*-butyl)-4´-hydroxyphenyl]propanoic acid (**1**) in solution of thionyl chloride gave 3,3´,5,5´-tetra(*tert*-butyl)-4,4´-dihydroxybiphenyl (**2**) and 3,3´,5,5´-tetra(*tert*-butyl)diphenoquinone (**3**), rather than expected 2-(acetylamino)-3-[3´,5´-di(*tert*-butyl)-4´-hydroxyphenyl]propanoyl chloride (Scheme 1). Formation of compounds **2** and **3** is usually observed under conditions of the oxidative condensation of 2,6-di(*tert*-butyl)phenol and its certain derivatives.[1—4] Therefore, it can be suggested that the formation of compounds **2** and **3** in the reaction of acid **1** with thionyl chloride involves a red-ox process.

Scheme 1



The ratio of the oxidation products of 2,6-di(*tert*-butyl)phenol or its derivatives depends on the nature of the oxidant, reaction conditions, and a possibility of forming complexes with proton-containing components. It can be suggested that under the oxidation conditions, acid **1** initially forms a phenoxyl radical, which recombinates to form compound **2**. In the excess of thionyl chloride, compound **2** is oxidized to diphenoquinone **3**.

^{1}H NMR spectra were recorded on a Bruker AvanceIII-500 (solvent $CDCl_3$).

Thionyl chloride (5 mL) was added to acid **1** (3.35 g, 0.01 mol) at 18 °C, after standing of the mixture for ~10 min, an excess of $SOCl_2$ was evaporated, water (30 mL) and toluene (40 mL) were added to the residue. A mixture of compounds **2** and **3** was obtained from the organic phase, reflux of which in EtOH (25 mL) gave a solution and an insoluble residue of the crystalline diphenoquinone **3**. The yield was 0.9 g (44.4%), m.p. 240—241 °C (*cf.* Ref. 4: m.p. 240—241 °C). ^{1}H NMR, δ: 1.40 (s, 36 H, Bu^t); 7.70 (s, 4 H, ring). After evaporation of the solvent from the ethanolic solution, the residue was recrystallized from *n*-hexane to obtain compound **2** (1.1 g, 53.6%), m.p. 184—185 °C (*cf.* Ref. 5: m.p. 185 °C). ^{1}H NMR, δ: 1.52 (s, 36 H, Bu^t); 5.19 (s, 2 H, OH); 7.29 (s, 4 H, Ar). The individuality of compounds **2** and **3** was confirmed by HPLC using a comparison with the authentic samples.

References

1. K. Ley, *Angew. Chem.*, 1958, **70**, 74.
2. L. Paquete, W. Farley, *J. Org. Chem.*, 1967, **32**, 2718
3. C. Cook, E. English, B. Wilson, *J. Org. Chem.*, 1958, **23**, 755.
4. E. Muller, A. Rieker, R. Mayer, K. Scheffler, *Lieb. Ann. Chem.*, 1961, **645**, 36.
5. M. Kharasch, B. Joshi, *J. Org. Chem.*, 1957, **22**, 1439.

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