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The formation of nitrogen-containing organic compounds in the transformations of 3,5-di-*tert*-butylpyrocatechol adsorbed on thin layers of SiO_2 in air

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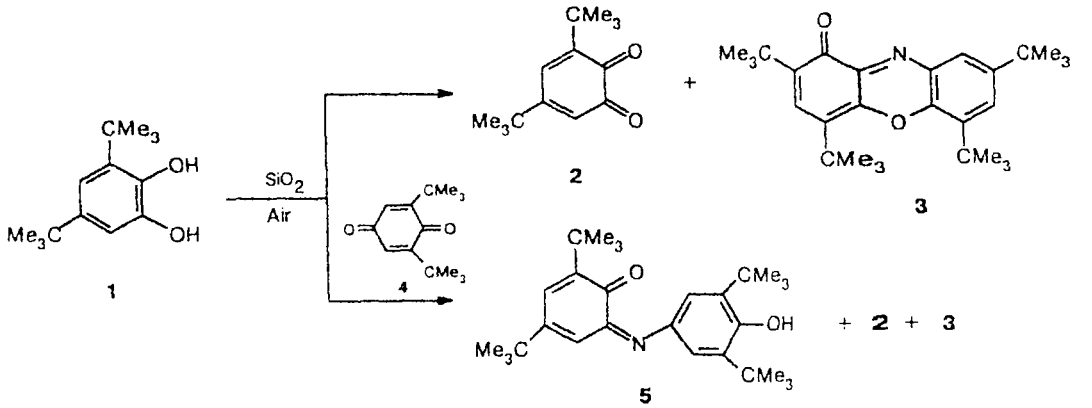
We discovered that 3,5-di-*tert*-butylpyrocatechol (**1**) adsorbed on thin layers of SiO_2 (0.15—0.20 mm, Silufol, Silufol UV-254 and UV-366, Kieselgel 60 F, and Silpearl plates containing no more than 0.02% of Fe; material of the supports: aluminum foil, plastic, glass; concentration of **1** 0.03—0.05 mg cm^{-2}) undergoes an oxidative transformation over a period of several days to give an intensely colored mixture of products. The process occurs in open air; in chambers with a flow of air passed successively through H_2SO_4, H_2O, and anhydrous $MgSO_4$; and in an N_2—O_2 (4 : 1) mixture. Preparative TLC of this mixture gives 3,5-di-*tert*-butyl-*ortho*-benzoquinone (**2**) (yield 20%, m.p. 113—114 °C (from hexane), which corresponds to published data[1]) and 1*H*-2,4,6,8-tetrakis-*tert*-butylphenoxazin-1-one (**3**) (yield up to 15%, m.p. 212 °C, the melting point of a mixture with the authentic sample prepared according to a published procedure[2] was undepressed). Found (%): N, 3.35. $C_{28}H_{39}NO_2$. Calculated (%): N, 3.31. ^{1}H NMR ($CDCl_3$) δ: 1.33, 1.36, 1.43, 1.47 (36 H, CMe_3); 7.38 (s, 1 H); 7.54 (d, 1 H), 7.83 (d, 1 H). In addition, a fraction consisting of several labile compounds with an overall nitrogen content of 2.8±0.5% was isolated. The joint transformation of compound **1** with 2,6-di-*tert*-butyl-*para*-benzoquinone (**4**) yields *N*-(4-hydroxy-3,5-di-*tert*-butyl)phenylimine of quinone **2** (**5**). This compound was identified by comparison with an authentic sample obtained from **2** and 2-amino-4,6-di-*tert*-butylphenol by a previously reported procedure.[3] The transformations of compound **1** are



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accelerated at higher temperatures and under UV irradiation.

The transformation of compound **1** in an atmosphere of an $Ar—O_2$ mixture (4 : 1) gives quinone **2** as the only product. In an atmosphere of N_2, compound **1** is stable over a long period.

These data altogether suggest that it is air that serves as the source of nitrogen for the formation of nitrogen-containing compounds in the transformations of **1** under consideration and that the formation of these products is associated with the oxidation of **1**.

The formation of nitrogen-containing compounds has also been found in the transformations on SiO_2 of other pyrocatechol derivatives, including those generated on SiO_2 *in situ*.

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