Letters to the Editor

Synthesis of 2,4-dibenzoyloxy-6-methylpyrimidine and its acylotropic transformations

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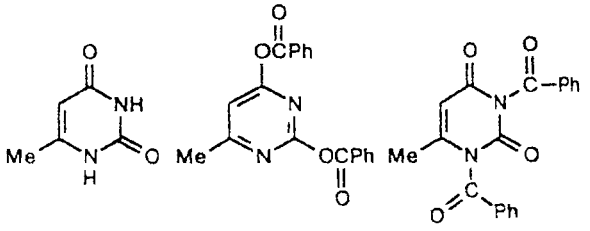
It is known that monohydroxypyrimidines are acylated at the O atom, while di- and trihydroxypyrimidines are acylated at the ring N atom.[1,2]

We were the first to show that it is possible to acylate dihydroxypyridines at the O atom. 6-Methyluracil **1**, unlike uracil and thymine, is not acylated by Ac_2O (140 °C, pyridine). We found that when PhCOCl is slowly added to compound **1** in MeCN in the presence of Et_3N at 10—15 °C, 2,4-dibenzoyloxy-6-methylpyrimidine (**2**) is formed. Under the same conditions, uracil and thymine are converted into their 1,3-dibenzoyl derivatives.[2] However, an increase in the velocity of the addition of PhCOCl or an increase in the temperature results in the formation of 1,3-dibenzoyl-6-methyluracil (**3**).



1 **2** **3**

At 10—15 °C, PhCOCl (28.2 g, 0.2 mol) was added dropwise at a rate of 8—10 drops per minute to a suspension of **1** (12.6 g, 0.1 mol) and Et_3N (20.2 g, 0.2 mol) in 100 mL of MeCN. The mixture was stirred for 1 h, the precipitate was filtered off, the solvent was evaporated *in vacuo*, and the residue was recrystallized from a hexane—benzene mixture to give 23.4 g (70%) of pyrimidine **2**, m.p. 79—80 °C. The results of elemental analysis correspond to the calculated data.

The IR spectrum of compound **2** (a solution in $CHCl_3$) exhibits a narrow band at 1757 cm^{-1} corresponding to ν(C=O), while the doublet at 1680 and 1705 cm^{-1} typical of the uracil fragment is absent.

O,O-Dibenzoyl derivative **2** is readily converted into its isomer **3**. This rearrangement occurs in the following instances: in the recrystallization of compound **2** from MeOH (yield of **3** is 95%, m.p. 139—140 °C, benzene); during heating in benzene containing a catalytic amount of PhCOCl (5 min, 80 °C, yield of **3** is 90%); during chromatography on Al_2O_3 ($CHCl_3$ as the eluent; yield 92%); or at temperatures above 110 °C (yield 92%). The 1600—1800 cm^{-1} range of the IR spectrum of compound **3** (a solution in $CHCl_3$) contains bands at 1675, 1710, 1740, and 1757 cm^{-1}.[2]

Unlike the dibenzoyl derivatives of uracil and thymine,[2] compounds **2** and **3** do not react with Ac_2O (140 °C) and do not eliminate one of the acyl groups during recrystallization from an alcoholic solution of HCl or during chromatography on Al_2O_3. We could not find conditions for the partial debenzoylation of compounds **2** and **3**. When these compounds are treated with methanolic MeONa, both benzoyl groups are eliminated.

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References

1. D. J. Brown, *The Pyrimidines*, Suppl. II, Intersci. Publ., New York, 252.

2. A. Novacek, D. Hesoun, and J. Gut, *Collect. Czech. Chem. Communs*, 1965, 30, 1890.

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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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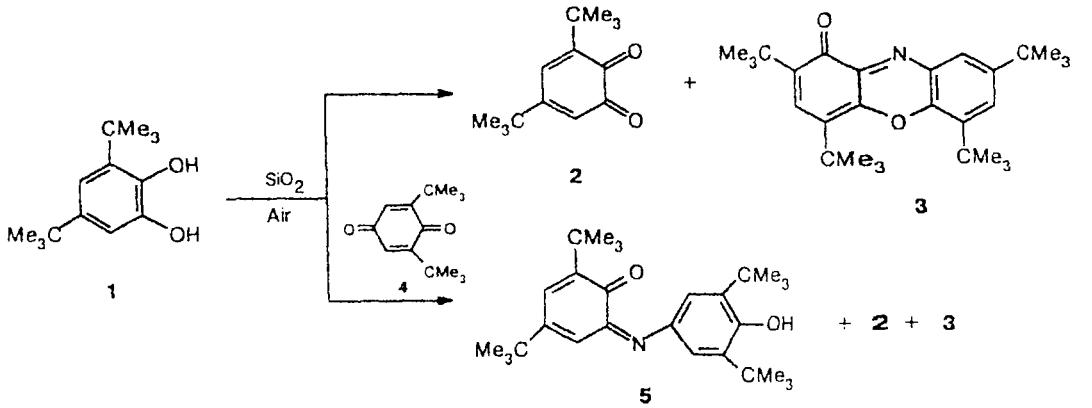
We discovered that 3,5-di-*tert*-butylpyrocatechol (**1**) adsorbed on thin layers of SiO_2 (0.15—0.20 mm, Silufol, Silufol UV-254 and UV-366, Kieselgel 60 F, and Silpearl plates containing no more than 0.02% of Fe; material of the supports: aluminum foil, plastic, glass; concentration of **1** 0.03—0.05 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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