Reaction of catechol with 1-hydroxyadamantane

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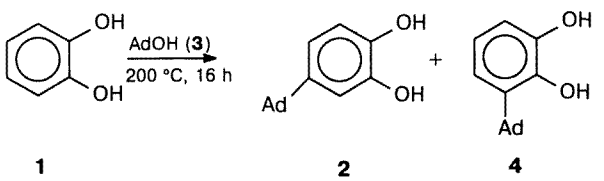
Friedel—Crafts alkylation of catechols in the presence of protic acids is known to give the corresponding 4-monoalkyl and 4,5-dialkyl derivatives. To obtain 3-mono- and 3,6-dialkylcatechols, reagents of the aluminum alkoxide—alkene type are used.[1,2]

Alkylation of catechol (**1**) with 1-bromoadamantane affords 4-(1′-adamantyl)catechol (**2**) as the only product.[3] Alkylation of compound **1** with 1-hydroxyadamantane (**3**) in the presence of BF_3 etherate, aside from catechol **2**, gives the product of disproportionation, namely, 1,3-di(3′,4′-dihydroxyphenyl)adamantane.[4]



1 **2** **4**

Ad = 1-Adamantyl

ortho-Alkylation of compound **1** has been scarcely studied, except for its reaction with isobutylene[5] and styrene[6] in the presence of titanium catecholate and aluminum phenoxide. At the same time, sterically hindered dihydric phenols containing bulky alkyl groups in the *ortho*-positions with respect to the hydroxyl groups are of obvious interest as intermediate compounds for synthesis of antioxidants and polyfunctional inhibitors of metal corrosion.[2]

It has been shown previously[7] that 1-hydroxyadamantane reacts with phenol at 150 °C without a catalyst (probably, phenol itself acts as a protic acid) giving 2- and 4-(1-adamantyl)phenols in ~3 : 2 ratio in a high yield. It could be suggested that adamantylation of compound **1** (see Refs. 3 and 4) yields initially both 3-(1′-adamantyl)catechol (**4**) and compound **2**, but the strong acids present in the reaction mixture isomerize **4** to the more stable **2**, and therefore compound **4** could not be isolated.

We carried out alkylation of compound **1** with alcohol **3** without a catalyst or solvent. Along with compound **2**, we actually isolated catechol **4**, the ratio between the isomers being 3.8 : 1.

Thus, we showed the possibility of preparing catechol **4** without a solvent or any additives.

A mixture of compounds **1** (0.88 g, 0.008 mol) and **3** (0.3 g, 0.002 mol) was sealed in a tube filled with argon. The mixture was heated for 16 h at 200 °C, washed with hot water, and dried. Column chromatography on 100×250 silica gel (elution with a chloroform : ether mixture, 33 : 1) gave:

catechol 2, yield 0.301 g (63 %), with a melting point corresponding to the published value.[4] ^{1}H NMR (100 MHz; tetramethylsilane; CD_2Cl_2), δ: 1.72—1.83—2.06 (15 H, adamantane moiety); 3.97 (2 H, OH group); 6.65—6.75—6.54 (3 H, benzene ring);

adamantane 4, yield 0.079 g (17 %), m.p. 204—206 °C. ^{1}H NMR (100 MHz; tetramethylsilane; C_6D_6), δ: 1.78—2.06—2.44 (15 H, adamantane moiety); 4.18 (s, 2 H, OH group); 6.24—6.50—6.70 (3 H, benzene ring). IR, ν/cm^{-1}: 3490 (OH group).

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