New rearrangement in the adamantylation reaction of 4-iodophenol and 4-iodoanisole

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A reaction of 2-iodophenol and 2-iodoanisole with 1-adamantanol in trifluoroacetic acid gives the corresponding 4-(1-adamantyl) derivatives. Similar adamantylation of 4-iodophenol and 4-iodoanisole is accompanied by migration of the iodine atom from *para*- to *ortho*-position, giving 4,6-di(1-adamantyl)-2-iodophenol and 4-(1-adamantyl)-2-iodoanisole, respectively, as the reaction products.

Key words: iodophenols, 1-adamantanol, alkylation, trifluoroacetic acid, electrophilic substitution, the Reverden rearrangement.

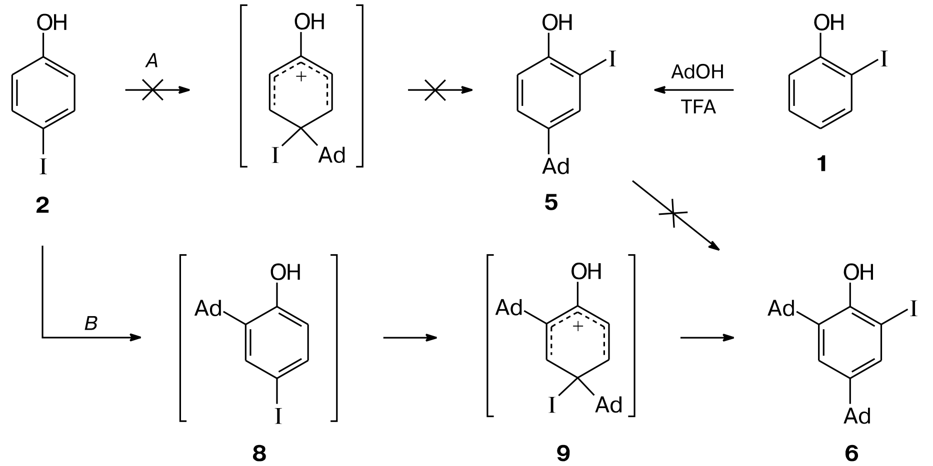
Nitration of halophenols and their ethers, as a rule, is not a simple process:[1,2] the nitro group usually substitutes for both the proton to give the corresponding nitro derivatives and the halogen atom at *para*-position with respect to the hydroxy or alkoxy group, which is accompanied by migration of the halogen atom to *ortho*-position. Such a reaction is known as the Reverden rearrangement.[3] Information on such a rearrangement of halophenols and their ethers in the alkylation reactions in the literature is absent.

We studied the reaction of 2-iodophenol (**1**), 4-iodophenol (**2**), 2-iodoanisole (**3**), and 4-iodoanisole (**4**) with 1-adamantanol in trifluoroacetic acid. Alkylation of phenol **1** at 20 °C and the ratio of reactants 1 : 1 furnished 4-(1-adamantyl)-2-iodophenol (**5**) as the reaction product (Scheme 1), which has been obtained earlier by iodination of 4-(1-adamantyl)phenol.[4]

Under similar conditions, phenol **2** is converted to 4,6-di(1-adamantyl)-2-iodophenol (**6**). Adamantylation of anisoles **3** and **4** leads to the same product, 4-(1-adamantyl)-2-iodoanisole (**7**) (Scheme 2).

Products of adamantylation of phenol **2** and ether **4** significantly differ. In the first case, a dialkylating product is formed already at the ratio of reactants 1 : 1 (see Scheme 1). Adamantylation of ether **4** gives the mono-

Scheme 1



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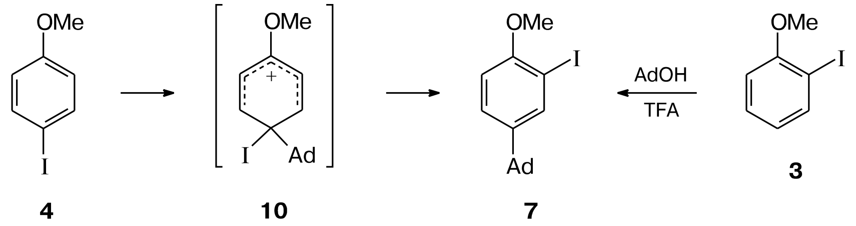
Scheme 2



alkylated product even at the ratio **4** : 1-AdOH = 1 : 2 (see Scheme 2).

Formation of product **6** (see Scheme 1) can be principally explained by the reaction taking pathways *A* or *B*. However, since phenol **5** is not alkylated with 1-AdOH in trifluoroacetic acid, the pathway *A* can be excluded, and the process apparently takes the pathway *B*.

The reaction can proceed according to the following mechanism. The first step includes adamantylation of phenol **2** to give compound **8**, *i.e.*, the adamantyl group commonly substitutes for the hydrogen atom. The second (fast) step includes an *ipso*-attack on the carbon atom bearing the iodine atom with the formation of σ-complex **9**, in which the iodine atom migrates to the *ortho*-position, that leads to phenol **6**. In the case of ether **4**, the first step includes an attack of the adamantyl cation to form the σ-complex **10**, which further rearranges to the ether **7**. The difference in the behavior of phenol **2** and anisole **4** in this reaction can be explained by greater steric hindrance, which is created by the methoxy group, as compared to that created by the hydroxy group. Alkylation of compound **3** leads to the usual substitution for the proton in *para*-position by the adamantyl group.

Special experiments showed that iodophenols and iodoanisoles under study do not undergo isomerization in trifluoroacetic acid.

To sum up, we found a new rearrangement of 4-iodophenol and 4-iodoanisole consisting in the migration of the iodine atom from position 4 to position 2 with simultaneous adamantylation of the aromatic ring.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker-Avance III-600 spectrometer in $CDCl_3$ (at the Community Center of the Krasnoyarsk Division of Siberian Branch of the RAS).

4-(1-Adamantyl)-2-iodophenol (5). A mixture of phenol **1** (0.220 g, 0.001 mol) and 1-AdOH (0.152 g, 0.001 mol) in CF_3COOH (2 mL) was kept at ~20 °C for 48 h, then poured into water, a precipitate was filtered off, washed with water, and dried. The yield was 0.32 g (90%), m.p. 110—112 °C (Pr^{i}OH) (see Ref. 4: m.p. 110—112 °C). ^{1}H NMR (600 MHz), δ: 1.73 (6 H, H(δ)), 1.83 (6 H, H(β)), 2.09 (3 H, H(γ)) (15 H, Ad); 5.09 (1 H, OH); 6.95 (d, 1 H, H(6), J = 8.5 Hz); 7.26 (dd, 1 H, H(5), J = 8.5 Hz, J = 2.3 Hz); 7.61 (d, 1 H, H(3), J = 2.3 Hz). ^{13}C NMR (150 MHz), δ: 28.81 (C(γ)); 35.50 (C(α)); 36.57 (C(δ)); 43.19 (C(β)); 85.77 (C(2)); 114.46 (C(6)); 126.82 (C(5)); 134.65 (C(3)); 145.90 (C(4)); 152.40 (C(1)).

Compounds **6** and **7** were obtained similarly.

4,6-Di(1-adamantyl)-2-iodophenol (6) was obtained from phenol **2** (0.220 g, 0.001 mol) and 1-AdOH (0.304 g, 0.002 mol) in CF_3COOH (4 mL). The yield was 0.350 g (72%), m.p. 240—242 °C (Pr^{i}OH). When the ratio **2** : 1-AdOH was 1 : 1, the yield was 50%. Found (%): C, 64.23; H, 6.42. $C_{26}H_{33}IO$. Calculated (%): C, 64.07; H, 7.02. ^{1}H NMR (600 MHz), δ: 1.81, 1.91, 2.15 (30 H, Ad); 5.40 (d, 1 H, OH, J = 0.5 Hz); 7.24 (dd, 1 H, H(5), J = 2.2 Hz, J = 0.5 Hz); 7.51 (d, 1 H, H(3), J = 2.2 Hz). ^{13}C NMR (150 MHz), δ: 29.43, 29.52 (C(γ)); 36.31, 38.29 (C(α)); 37.18, 37.51 (C(δ)); 40.75, 43.82 (C(β)); 90.45 (C(2)); 124.87 (C(5)); 132.67 (C(3)); 136.84 (C(6)); 145.49 (C(4)); 150.89 (C(1)).

4-(1-Adamantyl)-2-iodoanisole (7) was obtained from anisole **3** or anisole **4** (0.234 g, 0.001 mol) and 1-AdOH (0.152 g, 0.001 mol) in CF_3COOH (2 mL). The yields were: from anisole **3**, 89%, from anisole **4**, 75%, m.p. 128—129 °C. Found (%): C, 55.51; H, 5.69. $C_{17}H_{21}IO$. Calculated (%): C, 55.45; H, 5.74. ^{1}H NMR (600 MHz), δ: 1.80 (6 H, H(δ)), 1.90 (6 H, H(β)), 2.12 (3 H, H(γ)) (15 H, Ad); 3.90 (3 H, OMe); 6.81 (d, 1 H, H(6), J = 8.74 Hz); 7.32 (dd, 1 H, H(5), J = 2.35 Hz, J = 8.74 Hz); 7.78 (d, 1 H, H(3), J = 2.35 Hz). ^{13}C NMR (150 MHz), δ: 28.82 (C(γ)); 35.45 (C(α)); 36.58 (C(δ)); 43.18 (C(β)); 56.31 (OMe); 85.97 (C(2)); 110.50 (C(6)); 125.89 (C(5)); 136.26 (C(3)); 145.96 (C(4)); 155.88 (C(1)).

References

1. D. V. Nightingale, *Chem. Rev.*, 1947, **40**, 117.
2. K. V. Vatsuro, G. L. Mishchenko, *Imennye reaktsii v organicheskoi khimii* [*Named Reactions in Organic Chemistry*], Khimiya, Moscow, 1976, p. 346 (in Russian).
3. D. I. Makhon´kov, A. V. Cheprakov, I. P. Beletskaya, *Zh. Org. Khim.*, 1988, **24**, 2251 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1988, **24**].
4. V. I. Shvedov, O. A. Safonova, I. Ya. Korsakova, N. S. Bogdanova, I. S. Nikolaeva, V. V. Peters, G. N. Pershin, *Khim. Farm. Zh.*, 1980, **14**, 54 [*Pharm. Chem. J.* (*Engl. Transl.*), 1980, **14**].

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