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Adamantyl derivatives of pyrogallol

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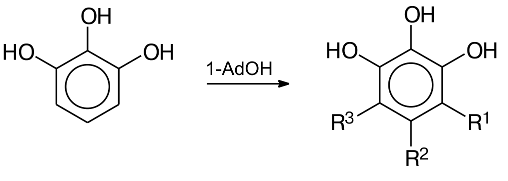
4-(1-Adamantyl)-, 5-(1-adamantyl)-, and 4,6-bis(1-adamantyl)pyrogallols were obtained by the reaction of adamantan-1-ol with pyrogallol in trifruoroacetic acid. The reaction of pyrogallol with adamantan-1-ol at 200 °C in a solvent-free medium without catalysts resulted in 5-(1-adamantyl)pyrogallol.

Key words: pyrogallol, adamantan-1-ol, alkylation, trifluoroacetic acid.

In continuation of research of adamantylation of polyatomic phenols,[1] we studied the reaction of pyrogallol with adamantan-1-ol in trifluoroacetic acid. The adamantylation of pyrogallol with 1-bromoadamantane has been performed earlier.[2] According to the data of the latter publication, a mixture of isomeric 4-(1-adamantyl)pyrogallol and 5-(1-adamantyl)pyrogallol formed that could not be separated. The composition and the structure of these compounds were tentatively established[2] on the basis of Stewart—Brigleb spatial model, IR spectra, and elemental analysis data. We found that heating of 1-BrAd with pyrogallol results only in 5-(1-adamantyl)pyrogallol.

We also found that pyrogallol reacts with adamantan-1-ol in CF_3COOH at 16 °C to form 4-(1-adamantyl)pyrogallol (**1a**), and at 85 °C to form 5-(1-adamantyl)pyrogallol (**1b**) (Scheme 1). Heating of compound **1a** at 85 °C in CF_3COOH results in its isomerization into compound **1b**. This means that isomer **1a** is a product of the kinetic control and isomer **1b** is a product of the thermodynamic control.

Scheme 1



1a—c

1	R1	R2	R3
a	Ad	H	H
b	H	Ad	H
c	Ad	H	Ad

When the double excess of adamantan-1-ol was used in the reaction at 8 °C, 4,6-bis(1-adamantyl)pyrogallol (**1c**) formed.

We obtained compound **1b** also by the reaction of adamantan-1-ol with pyrogallol at 200 °C using neither catalyst nor solvent. Apparently, the reaction is caused by the fact that the protonating agent is pyrogallol. It is known[3] that adamantan-1-ol reacts with pyrocatechol without a catalyst at 200 °C to form 4-(1-adamantyl)pyrocatechol (63%) and 3-(1-adamantyl)pyrocatechol (17%).

Intensive absorption bands (AB) at 2904 and 2848 cm^{-1} were present in the IR spectra of all the obtained adamantyl pyrogallol derivatives pertaining to stretching vibrations of the adamantane CH_2 groups. The AB at 1600—1500 cm^{-1} indicates the presence of an aromatic ring in the adamantyl derivatives. A comparison of the spectrum of the starting pyrogallol with the spectra of derivatives shows that the highest differences are observed in the region of stretching vibrations of the hydroxyl groups.

In the spectrum of compound **1b**, three poorly resolved broad AB are seen in this region with distinct maxima at 3351 and 3280 cm^{-1}, the maximum of the third high-frequency AB at 3524 cm^{-1} can be distinguished only upon deconvolution of the observed complicated spectral contour into individual components. All the three OH groups form fairly weak intermolecular hydrogen bonds of the H—O...H type. We should agree with the authors of the cited work[2] that the presence of the AB at 840 cm^{-1} in the spectrum indirectly proves the presence of the adamantyl group in position 5 of pyrogallol.

The spectrum in the region corresponding to vibrations of the hydroxyl groups of compound **1a** is quite different from that described above. Two AB observed at 3489 and 3448 cm^{-1} have half-widths of 36 and 40 cm^{-1},

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and a third broad AB at 3351 cm^{-1} has a half-width of 160 cm^{-1}. The low-frequency shift of the latter and its significant half-width indicates the involvement of the hydroxyl group in the formation of an intermolecular hydrogen bond. In our opinion, the highest-frequency AB at 3489 cm^{-1} characterizes stretching vibrations of the "free" hydroxyl group (it is identical to that in pyrogallol). We believe that the AB at 3448 cm^{-1} pertains to the stretching vibration of the OH group bound by an intermolecular hydrogen bond. The observed spectral pattern in the considered region is virtually analogous to that of *para*-substituted phenols.[4] The AB observed at 820 cm^{-1} confirms the substitution of adamantan-1-yl for hydrogen in position 4 of pyrogallol.[5] In the ^{1}H NMR spectrum of compound **1a**, the signals for the aromatic protons appear as two doublets at δ 6.33 and 6.51 with $J_{5,6}$ = 8.63 Hz; this shows that the protons are located in *ortho*-position to each other. In the spectrum of compound **1b**, there is a singlet at δ 6.44 which was ascribed to H(4) and H(6) with $J_{4,6}$ = 2.22 Hz (determined from ^{13}C satellites), such spin—spin coupling is typical of protons in *meta*-position. The signal for the proton H(5) of the aromatic part of compound **1c** appears as a singlet at δ 6.64.

Thus, convenient and selective methods for the synthesis of adamantyl derivatives of pyrogallol were developed. It was shown that at 130 °C, the reaction of 1-bromoadamantane with pyrogallol resulted in the product of the thermodynamic control, *viz.*, 5-(1-adamantyl)pyrogallol.

The reaction of pyrogallol with adamantan-1-ol without a solvent and a catalyst at 200 °C gives the same 5-(1-adamantyl)pyrogallol, water being a by-product. This is a typical example of a "green" chemistry reaction.

Experimental

IR spectra were recorded on a Bruker-Vector-22 Fourier-spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker—Avance III-600 spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz) (Scientific Center of SB RAS Krasnoyarsk) in acetone-d$_6$. The reaction products were purified by preparative TLC on Silufol (benzene : acetone, 9 : 1).

4-(1-Adamantyl)pyrogallol (1a). A mixture of pyrogallol (4 mmol) and 1-AdOH (1 mmol) in CF_3COOH (3 mL) and water (0.3 mL) was stirred for 15 min at 16 °C. The precipitate that formed was filtered off, washed with water, and dried. The yield was 0.190 g (73%), m.p. 220—221 °C. IR, ν/cm^{-1}: 3489, 3448, 3351 (OH); 2904, 2848 (CH_2, Ad). ^{1}H NMR (δ, *J*/Hz): 1.80 (6 H, H_δ); 2.05 (3 H, H_γ); 2.14 (6 H, H_β, Ad); 6.33 (d, 1 H, H(6)); 6.51 (d, 1 H, H(5), $J_{5,6}$ = 8.63); 6.37, 6.96, 8.02 (3 H, OH). ^{13}C NMR (δ): 29.15 (C_γ); 35.95 (C_α); 36.98 (C_δ); 40.82 (C_β, Ad); 105.73 (C(6)); 116.16 (C(5)); 128.11 (C(4)); 132.37 (C(2)); 145.27 (C(1)); 145.12 (C(3)) (pyrogallol). Found (%): C, 73.92; H, 7.69. $C_{16}H_{20}O_3$. Calculated (%): C, 73.82; H, 7.74.

5-(1-Adamantyl)pyrogallol (1b). ***A.*** A mixture of pyrogallol (1 mmol) and 1-AdOH (1 mmol) in CF_3COOH (2 mL) was heated for 3 h at 85 °C. The acid was removed, the reaction mixture was washed with water and dried. The yield was 0.17 g (66%), m.p. 213—215 °C.

B. A mixture of pyrogallol (3 mmol) and 1-AdOH (1 mmol) was heated in a sealed tube at 200 °C for 4 h, cooled, washed with water to remove pyrogallol, and dried. The yield was 0.185 g (71%), m.p. 213—215 °C.

C. A mixture of pyrogallol (3 mmol) and 1-BrAd (1 mmol) was heated for 15 min at 130 °C, cooled, washed with water to remove pyrogallol, and dried. The yield was 0.240 g (90%), m.p. 213—215 °C.

IR, ν/cm^{-1}: 3524, 3351, 3280 (OH); 2904, 2848 (CH_2, Ad). ^{1}H NMR (δ, *J*/Hz): 1.78 (6 H, H_δ); 1.84 (6 H, H_β); 2.05 (3 H, H_γ, Ad); 6.44 (2 H, H(4), H(6)); 7.05 (1 H, 2-OH); 7.56 (2 H, 1-OH, 3-OH) (pyrogallol). ^{13}C NMR (δ): 29.03 (C_γ); 35.28 (C_α); 36.98 (C_γ); 43.27 (C_β, Ad); 103.83 (C(4), C(6)); 130.30 (C(2)); 142.89 (C(5)); 145.26 (C(1), C(3)) (pyrogallol). Found (%): C, 73.54; H, 8.96. $C_{16}H_{20}O_3$. Calculated (%): C, 73.82; H, 8.79.

4,6-Bis(1-adamantyl)pyrogallol (1c). A mixture of pyrogallol (4 mmol) and 1-AdOH (2.5 mmol) in CF_3COOH (3 mL) was kept for 10 days at 8 °C. The precipitate was filtered off, washed, and dried. The yield was 0.277 g. Then compound **1a** was removed by washing with aqueous acetone (0.140 g, (63%)). The residuum was compound **1c**, 0.137 g (35%), m.p. 227—228 °C. IR, ν/cm^{-1}: 3534, 3503, 3342 (OH); 2904, 2848 (CH_2, Ad). ^{1}H NMR (δ): 1.80 (12 H, H_δ); 2.05 (6 H, H_γ); 2.15 (12 H, H_β, Ad); 6.64 (1 H, H(5)); 6.90 (2 H, 1-OH, 3-OH); 7.00 (1 H, 2-OH) (pyrogallol). ^{13}C NMR (δ): 29.24 (C_γ); 36.44 (C_α); 37.02 (C_δ); 40.86 (C_β, Ad); 115.13 (C(5)); 126.99 (C(4), C(6)); 132.21 (C(2)); 144.30 (C(1), C(3)) (pyrogallol). Found (%): C, 79.24; H, 8.75. $C_{26}H_{34}O_3$. Calculated (%): C, 79.15; H, 8.69.

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