Chemistry of Heterocyclic Compounds **2021**, *57*(3), 305–313

Reactions of β-carbonyl-substituted 4*H*-chromenes and 1*H*-benzo[*f*]chromenes with 5-aminopyrazoles

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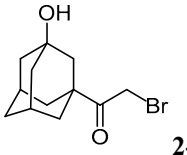
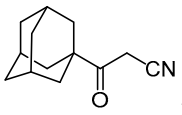
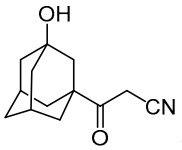
SUPPLEMENTARY INFORMATION



2-Bromo-1-(3-hydroxyadamantan-1-yl)ethan-1-one. Br_2 (1.3 ml, 26 mmol) was added dropwise to a solution of 1-(3-hydroxyadamantan-1-yl)ethan-1-one (5.00 g, 26 mmol) in EtOH (15 ml) under vigorous stirring at 60–65°C ensuring that discoloration of the solution after each drop of Br_2 occurs. The reaction mixture was kept at 0°C overnight. The obtained precipitate was filtered off and recrystallized from EtOAc. Yield 3.48 g (49%), colorless crystals, m. p. 93–94°C. IR spectrum, ν, см$^{-1}$: 3379, 3136 (OH), 2924, 2854 (CH Ad), 1705 (C=O), 1635, 1450, 1334, 1311, 1238, 1153, 1103, 1057, 1030, 987, 956, 918, 860, 632. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 1.57 (2H, t, *J* = 3.0); 1.66–1.76 (11H, m); 2.19–2.23 (2H, m); 4.34 (2H, s, CH_2Br). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 30.3 (2CH Ad); 33.9 (CH_2Br); 34.7 (CH_2 Ad); 36.8 ($2CH_2$ Ad); 43.4 ($2CH_2$ Ad); 44.9 (CH_2 Ad); 59.6 (C Ad); 69.1 (C–OH); 204.5 (C=O). Found, %: C 52.85; H 6.21. $C_{12}H_{17}BrO_2$. Calculated, %: C 52.76; H 6.27.



3-(Adamantan-1-yl)-3-oxopropanenitrile. A solution of NaCN (5.80 g, 118 mmol) in H_2O (25 ml) was added dropwise to a stirred solution of 1-(adamantan-1-yl)-2-bromoethan-1-one (10.0 g, 39 mmol) in 1,4-dioxane (50 ml) maintaining the temperature of the reaction mixture not higher than 25°C. The reaction mixture was stirred at room temperature for 5 h, then poured into cold H_2O (200 ml) and acidified with 20% aqueous AcOH to pH 5. The obtained precipitate was filtered off, washed with H_2O, and recrystallized from MeOH. Yield 6.90 g (87%), colorless crystals, m. p. 104–105°C (m. p. 98–100°C (petroleum ether)[1]). Spectral data of the obtained 3-(adamantan-1-yl)-3-oxopropanenitrile is in accordance with literature data.[1]

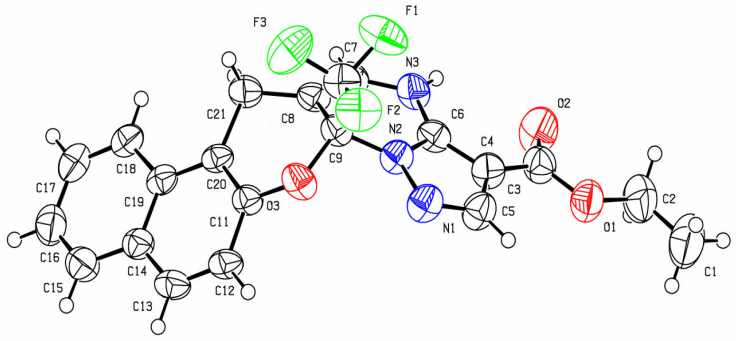


3-(3-Hydroxyadamantan-1-yl)-3-oxopropanenitrile. A solution of NaCN (1.61 g, 33 mmol) in H_2O (7 ml) was added dropwise to a stirred solution of 2-bromo-1-(3-hydroxyadamantan-1-yl)ethan-1-one (3.00 g, 11 mmol) in 1,4-dioxane (15 ml) maintaining the temperature of the reaction mixture not higher than 25°C The reaction mixture was stirred at room temperature for 5 h, then poured into cold H_2O (200 ml) and acidified with 20% aqueous AcOH to pH 5. The volatile components of the mixture were evaporated under reduced pressure, the residue was dissolved in H_2O (15 ml) and extracted with EtOAc. The extract was dried with anhydrous Na_2SO_4, and the obtained crude product was recrystallized from EtOAc. Yield 1.37 g (57%), colorless crystals, m. p. 125–126°C. IR spectrum, ν, см$^{-1}$: 3363 (OH), 2912, 2854 (CH Ad), 2256 (CN), 1708 (C=O), 1454, 1388, 1338, 1307, 1184, 1141, 1114, 1072, 1045, 987, 921, 839, 736. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.58–1.61 (2H, m, Ad); 1.66–1.76 (10H, m, Ad); 1.90 (1H, br. s, OH); 2.32 (2H, br. s, Ad); 3.60 (2H, s, CH_2CN). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.6 ($\underline{C}H_2CN$); 30.1 (2CH Ad); 34.8 (CH_2 Ad); 37.0 ($2CH_2$ Ad); 44.1 ($2CH_2$ Ad); 45.3 (CH_2 Ad); 50.2 (C Ad); 68.3 (C–OH); 114.0 (CN); 201.0 (C=O). Found, %: C 71.22; H 7.75; N 6.25. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

1. Shiryaev, A. K.; Belen´kaya, R. S.; Shiryaev, V. A.; Rybakov, V. B.; Klimochkin, Y. N. *Russ. Chem. Bull., Int. Ed.* **2015**, *64*, 2966. [*Изв. АН, Сер. хим.* **2015**, 2966.]

Crystallographic Data

Table 1. Crystal data and structure refinement for compound **4g**



CCDC Number	2038689
Empirical formula	$C_{21}H_{16}F_3N_3O_3$
Formula weight	415.37
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.55000(10)
b/Å	8.1588(2)
c/Å	36.3815(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1944.23(8)
Z	4
ρ_{calc}g/cm^3	1.419
μ/mm^{-1}	0.992
F(000)	856.0
Crystal size/mm^3	0.345 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.858 to 152.466
Index ranges	$-5 \le h \le 8$, $-10 \le k \le 10$, $-44 \le l \le 45$
Reflections collected	11560
Independent reflections	3961 [R_{int} = 0.0324, R_{sigma} = 0.0277]
Data/restraints/parameters	3961/0/284
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1518
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1563
Largest diff. peak/hole / e Å^{-3}	0.24/-0.20