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Selective Hydroxylation of Diamantane with 2,3,4,5,6-Pentafluoroperbenzoic Acid in the Presence of Molibdenum Complexes

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Abstract—Oxidation of diamantane with 2,3,4,5,6-pentafluoroperbenzoic acid catalyzed with complexes $MoO(O_2)\cdot 2QOH$, $MoO(O_2)(H_2O)_2$ proceeds selectively affording diamantan-1-ol and diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate.

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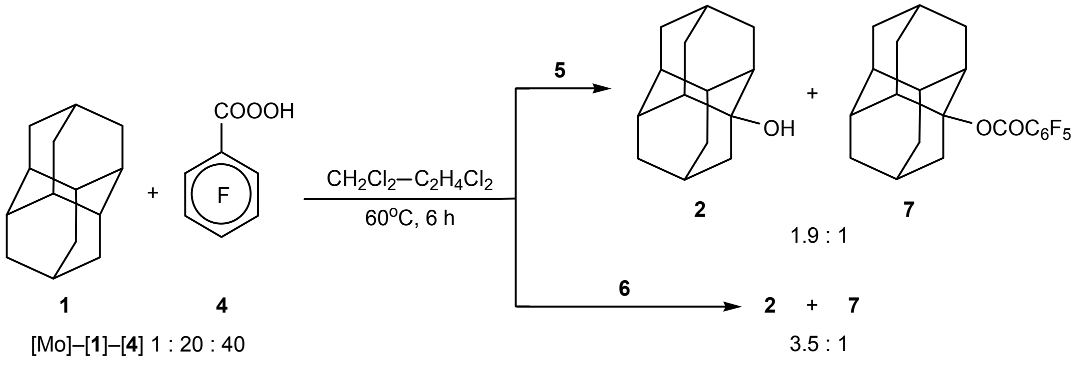
In the molecule of the second specimen of the homologous series of diamondoids, diamantane **1**, two types of tertiary carbon atoms are present: 6 medial (C^1, C^2, C^6, C^7, C^{11}, C^{12}) and 2 apical (C^4, C^9) atoms. Because of diverse surroundings they possess different reactivity coming out in the synthesis of monosubstituted derivatives of compound **1**, which usually form as a mixture of isomeric products of substitution in the positions *1* and *4*, the former prevailing [1]. This occurs at the preparation of diamantanols by diamantane **1** hydroxylation with various oxidants. The ratio of isomers, diamantane-1- and -4-ols **2** and **3**, which are very difficultly separable, depends on the nature of the oxidant.

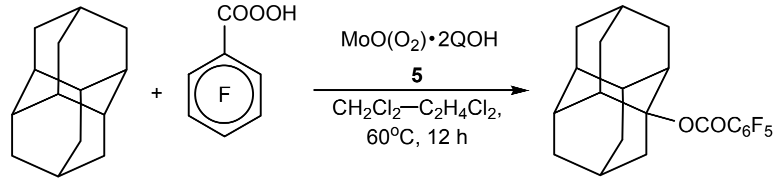
At diamantane **1** oxidation with oxygen in the conditions of radical initiation using *N*-hydroxyphthalimide and AIBN a mixture formed of compounds **2** and **3** in a ratio 3 : 1 [2]. The oxidation with lead tetraacetate in the environment of $CF_3COOH–CH_2Cl_2$ led to the formation of the mixture of compounds **2** and **3** in a ratio 9 : 1. When the diamantane **1** oxidation with $Pb(OAc)_4$ is carried out with adding LiBr the fraction of isomer **3** grows to 14% [3]. The oxidation of diamantane **1** with *m*-chloroperbenzoic acid proceeds sufficiently selectively giving compounds **2** and **3** in a ratio 8 : 1 [4].

In the search for a reagent for the selective hydroxylation of diamantane **1** we studied its oxidation with 2,3,4,5,6-pentafluoroperbenzoic acid **4** in the presence of catalysts, molybdenum complexes. Peracid **4** was first obtained and investigated in [5, 6], and it was successfully used for adamantane hydroxylation [7].

Scheme 1.



Scheme 2.

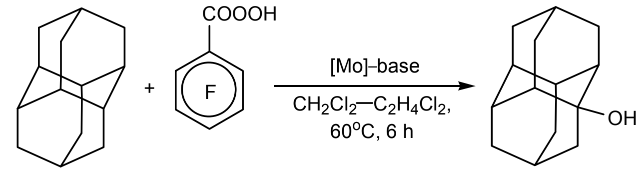


1 **4** **7**

[**5**]–[**1**]–[**4**] 1 : 20 : 80

Peracid **4** (6% O_{act}) in the presence of molybdenum oxo-peroxo complexes $MoO(O_2)·2QOH$ **5** (QOH is 8-hydroxyquinoline) and $MoO(O_2)(H_2O)_2$ **6** oxidizes diamantane **1** (60°C, 6 h) giving diamantan-1-ol **2** and diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7**, and their yields depend on the catalyst nature and the reaction conditions (Scheme 1).

Scheme 3.



1 **4** **2**

[Mo]–[**1**]–[**4**]–[base] 1 : 20 : 40 : 20

[Mo]	Base	Yield **2**, %
5	$NaHCO_3$	61
	K_2CO_3	49
	NaOAc	68
6	NaOAc	71

In the presence of $MoO(O_2)·2QOH$ **5** the conversion of diamantane **1** reached 52%, in the presence of $MoO(O_2)(H_2O)_2$ **6**, 40%, and in the presence of $Mo(CO)_6$ and $MoO_2(acac)_2$ the conversion of compound **1** did not exceed 5%. Due to the limited solubility of complexes **5** and **6** in the most organic solvents the experiments were performed in the mixture dichloromethane–1,2-dichloroethane. In this mixture complexes **5** and **6** are completely soluble at 30–40°C.

The reaction time increased to 12 h did not result in a larger yield of alcohol **2**. At 30°C the yield of compound **2** was 30%. At the oxidation of diamantane **1** with 4-fold excess of peracid **4** (60°C, 12 h) in the presence of complex **5** the only reaction product was diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7** in a 50% yield (Scheme 2).

It is presumable that the cause of the incomplete conversion of diamantane **1** is the decomposition of complexes **5** and **6** by the action of strong 2,3,4,5,6-pentafluorobenzoic acid formed in the course of the reaction. Evidently, the deactivating effect of peracid **4** may be reduced with bases. Actually, the addition of

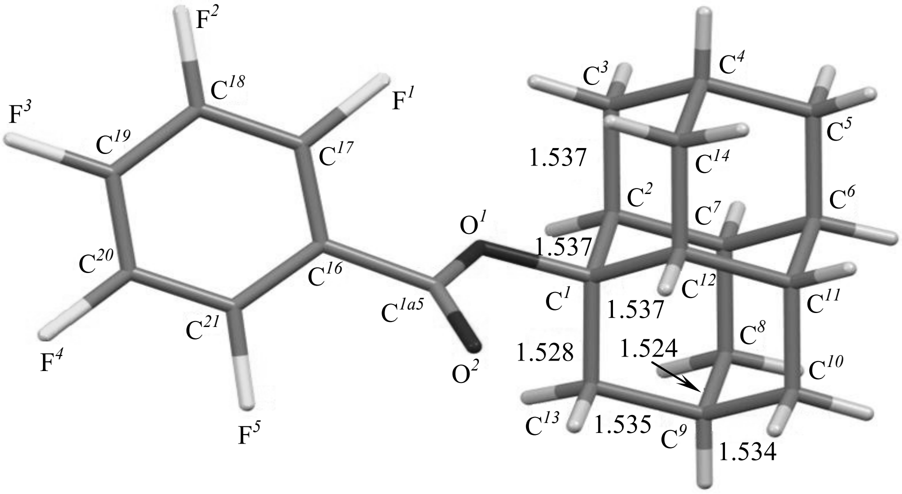


Fig. 1. Geometry of diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7** from XRD data.

Table 1. Bond lengths in the molecule of diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7**

Bond	*d*, Å	Bond	*d*, Å
$O^{1}–C^{1}$	1.4861(17)	$C^{12}–C^{11}$	1.540(2)
$O^{1}–C^{15}$	1.3271(18)	$C^{12}–C^{14}$	1.5380(19)
$O^{2}–C^{15}$	1.2020(18)	$C^{13}–C^{1}$	1.5284(17)
$C^{2}–C^{1}$	1.537(2)	$C^{13}–C^{9}$	1.535(2)
$C^{2}–C^{3}$	1.5370(18)	$C^{15}–C^{16}$	1.508(2)
$C^{2}–C^{7}$	1.538(2)	$C^{16}–C^{17}$	1.3877(19)
$C^{3}–C^{4}$	1.535(2)	$C^{16}–C^{21}$	1.385(2)
$C^{4}–C^{14}$	1.528(2)	$C^{18}–C^{17}$	1.381(2)
$C^{4}–C^{5}$	1.529(3)	$C^{18}–C^{19}$	1.379(3)
$C^{6}–C^{11}$	1.543(2)	$C^{19}–C^{20}$	1.371(2)
$C^{6}–C^{5}$	1.527(3)	$C^{21}–C^{20}$	1.384(2)
$C^{7}–C^{6}$	1.540(2)	$F^{1}–C^{17}$	1.337(2)
$C^{7}–C^{8}$	1.535(2)	$F^{2}–C^{18}$	1.3370(17)
$C^{9}–C^{8}$	1.524(3)	$F^{3}–C^{19}$	1.339(2)
$C^{9}–C^{10}$	1.534(3)	$F^{4}–C^{20}$	1.339(2)
$C^{11}–C^{10}$	1.534(2)	$F^{5}–C^{21}$	1.3369(17)
$C^{12}–C^{1}$	1.5372(18)		

$NaHCO_3$, K_2CO_3, or NaOAc results in a considerable increase in the yield of alcohol **2** (68%) with simultaneously the selectivity growing to 100% (Scheme 3).

The structure of diamantan-1-ol **2** was established from the ^{1}H, ^{13}C NMR spectra and by the comparison of the ^{13}C NMR spectra with published data [8, 9]. Another proof of the selective oxidation of compound **1** furnishing diamantan-1-ol **2** is provided by X-ray diffraction (XRD) analysis of ester **7**.

According to XRD data compound **7** forms colorless crystal of triclinic crystal system (Fig. 1). Fragment C_6F_5CO is turned around the $C^{1}–O^{1}$ bond by a torsion angle $O^{1}C^{15}C^{16}C^{21}$ –55.47(3)°. The bond lengths and bond angles in ester **7** are compiled in Tables 1 and 2.

To establish the effect of the ester substituent on the diamantane scaffold we performed XRD analysis of diamantane **1** (Fig. 2).

As seen from the comparison of the bond distances in compounds **1** and **7** (Tables 1 and 3) the influence of the residue of 2,3,4,5,6-pentafluorobenzoate on the bond lengths in the diamantane scaffold is negligible.

Therefore 2,3,4,5,6-pentafluoroperbenzoic acid in the presence of complexes $MoO(O_2)\cdot 2QOH$ **5**, $MoO(O_2)(H_2O)_2$ **6** selectively oxidized diamantane **1**

Table 2. Bond angles in the molecule of diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7**

Angle	φ, deg	Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$C^{15}O^{1}C^{1}$	121.00(10)	$F^{1}C^{17}C^{18}$	118.01(13)	$O^{1}C^{15}C^{16}$	110.38(11)	$C^{4}C^{14}C^{12}$	110.03(12)
$C^{1}C^{12}C^{11}$	107.03(11)	$C^{18}C^{17}C^{16}$	121.72(15)	$O^{2}C^{15}O^{1}$	127.79(15)	$C^{8}C^{9}C^{13}$	109.46(14)
$C^{1}C^{12}C^{14}$	110.82(12)	$C^{14}C^{4}C^{3}$	109.09(14)	$O^{2}C^{15}C^{16}$	121.82(14)	$C^{8}C^{9}C^{10}$	110.02(16)
$C^{14}C^{12}C^{11}$	110.53(13)	$C^{14}C^{4}C^{5}$	109.36(16)	$C^{2}C^{7}C^{6}$	108.54(13)	$C^{10}C^{9}C^{13}$	108.89(13)
$C^{1}C^{2}C^{7}$	107.67(11)	$C^{5}C^{4}C^{3}$	109.40(14)	$C^{8}C^{7}C^{2}$	110.92(13)	$F^{3}C^{19}C^{18}$	120.07(16)
$C^{3}C^{2}C^{1}$	111.08(11)	$C^{7}C^{6}C^{11}$	107.88(14)	$C^{8}C^{7}C^{6}$	110.75(14)	$F^{3}C^{19}C^{20}$	119.79(18)
$C^{3}C^{2}C^{7}$	110.66(13)	$C^{5}C^{6}C^{7}$	110.32(14)	$C^{4}C^{3}C^{2}$	109.28(12)	$C^{20}C^{19}C^{18}$	120.13(17)
$C^{1}C^{13}C^{9}$	108.95(13)	$C^{5}C^{6}C^{11}$	110.88(14)	$C^{17}C^{16}C^{15}$	122.92(13)	$C^{9}C^{8}C^{7}$	109.06(13)
$O^{1}C^{1}C^{12}$	111.76(10)	$C^{12}C^{11}C^{6}$	108.73(13)	$C^{21}C^{16}C^{15}$	119.88(12)	$F^{4}C^{20}C^{21}$	120.40(16)
$O^{1}C^{1}C^{2}$	104.16(10)	$C^{10}C^{11}C^{12}$	110.92(14)	$C^{21}C^{16}C^{17}$	117.08(15)	$F^{4}C^{20}C^{19}$	120.05(18)
$O^{1}C^{1}C^{13}$	109.21(11)	$C^{10}C^{11}C^{6}$	110.66(14)	$F^{2}C^{18}C^{17}$	120.30(17)	$C^{19}C^{20}C^{21}$	119.54(16)
$C^{12}C^{1}C^{2}$	108.95(12)	$F^{5}C^{21}C^{16}$	120.07(15)	$F^{2}C^{18}C^{19}$	120.10(17)	$C^{11}C^{10}C^{9}$	109.36(13)
$C^{13}C^{1}C^{12}$	112.01(11)	$F^{5}C^{21}C^{20}$	118.01(14)	$C^{19}C^{18}C^{17}$	119.60(14)	$C^{6}C^{5}C^{4}$	110.02(14)
$C^{13}C^{1}C^{2}$	110.47(11)	$C^{20}C^{21}C^{16}$	121.92(14)	$F^{1}C^{17}C^{16}$	120.26(15)		

Table 3. Bond lengths and bond angles in the molecule of diamantane **1**

Bond	*d*, Å	Bond	*d*, Å
C^1–C^2	1.5317(10)	C^{10}–C^{11}	1.5327(13)
C^1–C^{12}	1.5317(10)	C^{12}–C^{14}	1.5327(13)
C^2–C^7	1.5317(10)	C^3–C^4	1.5250(12)
C^6–C^7	1.5317(10)	C^4–C^5	1.5250(12)
C^{11}–C^{12}	1.5317(10)	C^4–C^{-14}	1.5250(12)
C^1–C^{13}	1.5327(13)	C^9–C^8	1.5250(12)
C^2–C^3	1.5327(13)	C^9–C^{10}	1.5250(12)
C^5–C^6	1.5327(13)	C^9–C^{13}	1.5250(12)
C^7–C^8	1.5327(13)		
Angle	φ, deg	Angle	φ, deg
$C^2C^1C^{12}$	108.57(7)	$C^3C^4C^{14}$	109.18(6)
$C^2C^1C^{13}$	110.42(9)	$C^5C^4C^{14}$	109.18(6)
$C^{12}C^1C^{13}$	110.27(9)	$C^4C^3C^2$	109.79(8)
$C^3C^4C^5$	109.18(6)		

to form diamantan-1-ol **2** and diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7** opening a simple and promising way to the synthesis of difficultly available diamantine derivatives substituted in the position *1*.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{19}F NMR spectra were registered on a spectrometer Bruker Avance-III 500 Ascend, operating frequencies 500.17 (^{1}H) and 125.78 (^{13}C) MHz from solutions in $CDCl_3$. Mass spectra were measured on an instrument Shimadzu GCMS-QP2010Plus (capillary column SPB-5 30 × 0.25 mm, carrier gas helium, ramp from 40 to 300°C, heating rate 8 deg/min, vaporizing temperature 280°C, ion source temperature 200°C, ionizing energy 70 eV). Elemental analysis of samples was determined on an analyzer Carlo Erba 1106. Reactions progress was monitored and the purity of obtained compounds checked by GLC on a chromatograph Shimadzu GC-9A, GC-2014 [column 2 m × 3 mm, stationary phase silicone SE-30 (5%) on Chromaton N-AW-HMDS, ramp from 50 to 270°C, heating rate 8 deg/min, carrier gas helium (47 mL/min)].

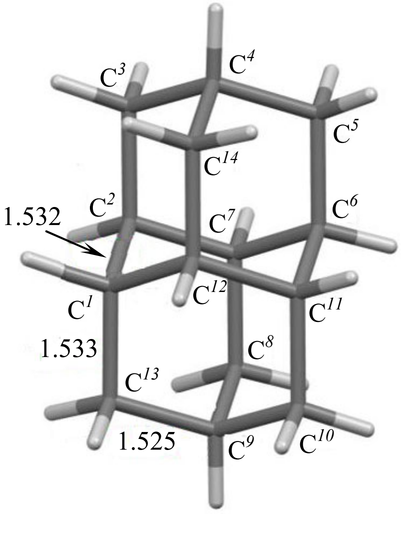


Fig. 2. Geometry of diamantane **1** from XRD data.

The XRD analysis of diamantane **1** and diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate **7** was carried out on an automatic four-circle diffractometer XCalibur Eos (graphite monochromator, MoK_α-radiation, λ 0.71073 Å, ω-scanning, $2\theta_{max}$ 62°). The collection and processing of data was performed using software CrysAlisPro Oxford Diffraction Ltd. The structures were solved by the direct method and refined by full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were localized by the difference Fourier synthesis and included in the refinement with fixed thermal parameters and positions. The calculations were performed applying SHELX program [10]. Cif-files are deposited in Cambridge Crystallographic Data Center under the numbers CCDC 935374 (**1**) and CCDC 1469654 (**7**). The data are available free on request at the address CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk) or on the site http://www.ccdc.cam.ac.uk/data_request/cif.

Oxo–peroxo molibdenum complexes $MoO(O_2)\cdot 2QOH$ **5** and $MoO(O_2)(H_2O)_2$ **6** were synthesized by procedures [11, 12] respectively. 2,3,4,5,6-Pentafluoroperbenzoic acid **4** was prepared by ozonization of commercial 2,3,4,5,6-pentafluorobenzaldehyde by the method [5, 6].

Diamantan-1-ol (2). To a mixture of 0.013 mmol of catalyst **5** and **6**, 0.05 g (0.26 mmol) of diamantane **1**, and 0.013 mmol of a base ($NaHCO_3$, K_2CO_3, NaOAc) in 2 mL of 1,2-dichloroethane at 30–50°C was added dropwise 0.12 g (0.52 mmol) of peracid **4** in 2 mL of CH_2Cl_2 within 1.5 h. On completing the addition of acid **4** 0.013 mmol of a base was added, and the mixture was stirred for 4.5 h at 60°C. The organic layer was decanted and filtered through a bed of Al_2O_3 (eluent $CHCl_3$), the inorganic phase was treated with 0.1 N H_2SO_4 and was extracted with $CHCl_3$. Both organic phases were combined, the solvents were evaporated. The reaction products were isolated by column chromatography on silica gel (60–200 μm, 60 Å), eluents: hexane, ethyl acetate. Yield 71%, white crystals, R_f 0.67 (EtOAc), mp 291–292°C (292–294°C [13]). ^{1}H NMR spectrum, δ, ppm: 1.25 br.s (1H, OH), 1.43–1.50 m (2H, CH_2), 1.58–1.74 m (13H, $5CH_2$, 3CH), 1.95 s (1H, CH), 2.04–2.10 m (2H, 2CH), 2.14–2.17 m (1H, CH). ^{13}C NMR spectrum, δ, ppm: 25.37 (C^{4}), 30.52 (C^{9}), 32.62 ($C^{3,14}$), 36.80 (C^{6}), 37.60 ($C^{8,10}$), 38.06 (C^{5}), 40.03 ($C^{7,11}$), 43.45 ($C^{2,12}$), 46.46 (C^{13}), 70.92 (C^{1}). Mass spectrum, m/z (I_{rel}, %): 204 (18.4) $[M]^+$, 186 (77.2), 130 (44.2), 129 (33.9), 95 (96.6), 94 (100), 91 (36.8), 79 (27.2). Found, %: C 81.97; H 9.90. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.87. M 204.31.

Diamantan-1-yl 2,3,4,5,6-pentafluorobenzoate (7). To a mixture of 0.013 mmol of $MoO(O_2)\cdot 2QOH$ **5**, 0.05 g (0.26 mmol) of diamantane **1** in 2 mL of 1,2-dichloroethane at 30–50°C was added dropwise a solution of 0.12 g (0.52 mmol) of peracid **4** in 1.5 mL of CH_2Cl_2 within 1.5 h, and the mixture was stirred for 4.5 h at 60°C. Then was added more 0.12 g of acid **4** in 1.5 mL of CH_2Cl_2 within 1.5 h at 30–50°C, and the mixture was stirred additionally for 4.5 h. After 12 h the reaction mixture was filtered through a bed of Al_2O_3 (eluent $CHCl_3$). The reaction products were isolated by column chromatography on silica gel (60–200 μm, 60 Å), eluents: hexane, chloroform. Yield 50%, white crystals, R_f 0.63 ($CHCl_3$), mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 1.50–1.53 m (2H, $2CH_2$), 1.63–1.65 m (2H, $2CH_2$), 1.71–1.79 m (4H, 2CH, $2CH_2$), 2.06–2.10 m (4H, 2CH, $2CH_2$), 2.11–2.20 m (1H, CH), 2.28–2.29 m (2H, CH_2,), 2.42 s (2H, 2CH). ^{13}C NMR spectrum, δ, ppm: 24.92 (C^{4}), 30.39 (C^{9}), 32.49 ($C^{3,14}$), 36.66 (C^{6}), 37.11 ($C^{8,10}$), 37.95 (C^{5}), 40.28 ($C^{2,12}$), 40.52 ($C^{7,11}$), 40.69 (C^{13}), 157.60 (C^{15}). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: −160.76 ($F^{2,6}$), –105.70 (F^{4}), –139.52 ($F^{3,5}$). Mass spectrum, m/z (I_{rel}, %): $[M]^+$ is absent, 212 (0.5), 186 (100), 130 (12), 129 (19.7), 95 (28.8), 94 (20.3), 91 (23.6), 79 (14.4). Found, %: C 63.20; H 4.92. $C_{21}H_{19}F_5O_2$. Calculated, %: C 63.31; H 4.81. M 398.36.

Crystallographic data: $C_{21}H_{19}F_5O_2$. M 398.37, a 7.7448(6), b 9.9926(8), c 12.7617(12) Å, V 858.25(14) Å^3, Z 2, d_{calc} 1.541 g/cm^3, R 0.0524, wR_2 0.1537.

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