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NO_2^+-Containing Reagents in the Electrophilic and Oxidative Addition to Propellanic C-C Bond [1]

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Abstract: Reactions of several propellanes with 100% HNO_3 and nitronium salts were studied. 1,3-Dehydroadamantane (**1**) in accordance with the Ad_E - scheme formed 1-nitroxyadamantane (**4**) with HNO_3, 1-nitroxy-3-nitroadamantane (**6**) with NO_2NO_3, and 1-fluoro-3-nitroadamantane (**5**) with NO_2BF_4. Considerably stable in electrophilic media 3,6-dehydrohomoadamantane (**2**) under the same conditions underwent oxidative addition (Ad_{Ox}) and formed 3,6-disubstituted homoadamantane derivatives: dinitroxy- (**7**) with HNO_3 or NO_2NO_3/CH_2Cl_2, diacetamino- (**11**) with NO_2BF_4/CH_3CN, difluoro- (**14**) with NO_2BF_4/EtOAc. The reactions of 4-methyl-3,6-dehydrohomoadamantane (**19**) proceeded according to a similar Ad_{Ox}-scheme, but the homoadamantane nucleus was rearranged into adamantane and compounds (**20**)-(**24**) were formed. 1,5-Dehydrobicyclo[3.3.1]nonane (**3**) like **2** formed 1,5-disubstituted bicyclo[3.3.1]nonanes in the course of oxidative addition. The scheme of *backside* oxidative addition to the propellanic C-C bond is proposed. MNDO-calculations of propellanes (**1**)-(**3**) were carried out and the protonation as a model process of electrophilic addition was studied using energy/C-C...H^+ distance relationships. It was concluded that the nonelectrophilic nature of **2** and **3** interactions with HNO_3 and nitronium salts is a result of their higher stability in electrophilic media.

INTRODUCTION

Among different methods of alkane functionalization oxidation is the most important. Nitrogen-containing oxidants were the first to refute the opinion of alkanes as completely unreactive substances.[2] Unfortunately, the low selectivity of homolytic C-H nitration and C-C nitrolysis in alkane series decreases their utility in preparative alkane chemistry. Research work on the electrophilic alkane functionalization by means of nitronium salts[3] considerably advanced this field. Fair selectivity is achieved from the sharp decrease of σ-bond reactivity along the series *tert*.C-H>C-C> *sec*.C-H.>*prim*.C-H[4] resulting in successful development of *tert*.C-H functionalization of alkanes, mainly cage compounds with 100% nitric acid[5] and nitronium reagents.[6] Nevertheless the interpretation of reaction mechanisms is difficult in this case because:

i) reactions are not high selective, sometimes the solvent or the nucleophilic part of the reagent takes part in the formation of reaction products

ii) ambident properties of electrophile

iii) difficulty of identifying the nature of a leaving group in the case of hydrogen substitution

iv) C-H bonds permit both *backside* and *frontside* attack of the reagent

v) oxidative mechanism cannot be excluded, NO_2^+ possesses both electrophilic and oxidative properties.

The above problems are, to some extend, also characteristic of other reactions of alkanes, such as halogenation,[7] carbonylation,[8] heterolysis in superacidic media,[9] etc.

As C-H and σ_{C-C} bond activation possess some common features,[10] propellane hydrocarbons[11] seem to be promising substrates for the study of the alkanes reactions with nitronium reagents. They undergo the addition of electrophilic reagents to the strained C-C bond via a highly selective route through the stereochemically definite *backside* attack[11] which does not compete with the C-H substitution reaction. Propellanes also have a unique possibility of σ_{C-C} -bond reactivity variation by changing ring sizes.[12] Methods for the determination of the border between different addition reaction mechanisms are needed. In the present communication the results of studying the reactions of propellane hydrocarbons with 100% nitric acid and nitronium salts in different media are discussed.

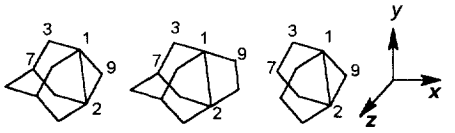
RESULTS AND DISCUSSION.

Substrates. Hydrocarbons **1-3** (SCHEME 1) with a characteristic propellanic C-C bond were chosen as substrates. According to the MNDO[13] calculations (MOPAC-7) and data on theirs reactivity towards electrophiles, the C-C bonds varies considerably under small structural differences. The heat of formation ΔH_f, bond lengths (l), and electron densities on atoms (δ) were estimated (Table). These data demonstrate substantial differences between molecules **1-3** concerning molecular strain, quaternary carbon atom distances and electron densities and, most substantial, AO contributing to HOMO (SCHEME 1). HOMO of 1,3-dehydroadamantane (**1**) is mainly formed by substantial contribution of p_x and p_y AO of cyclopropane carbon atoms and is typical for propellanes with a three-membered cycle.[14] HOMO of 3,6-dehydrohomoadamantane (**2**) is mainly formed by contribution of P_z AO of cyclobutane and cage fragment carbon atoms

Table. Some MNDO-calculations data for hydrocarbons **1-3**

Parameter \ Substrate	1	2	3
ΔH_f, kJ/mol	496.5	350	-1.80
$l_{C^1-C^2}$, Å	1.65	1.64	1.56
δc^1	-0.20	-0.11	-0.16

SCHEME 1



1 **2** **3**

$$\Psi_{HOMO} = 0.36\varphi_x^1 - 0.5\varphi_y^1 - 0.23\varphi_x^9 \quad (1)$$

$$\Psi_{HOMO} = -0.23\varphi_z^1 - 0.17\varphi_y^3 + 0.31\varphi_z^3 + 0.28\varphi_y^7 \quad (2)$$

$$\Psi_{HOMO} = 0.34\varphi_x^1 - 0.46\varphi_y^1 - 0.27\varphi_x^9 \quad (3)$$

and this exceeds the bound differences caused by the nature of cyclopropane and cyclobutane.[15] Based on these data, quite different chemical properties of **1** and **2** could be expected. For 1,5-dehydrobicyclo[3.3.1]nonane (**3**) the propellanic nature of HOMO similar to that of **1**, the propellane bond length typical for cyclopropanes[16] and considerable decrease in molecular strain energy should be pointed out.

For propellanes **1-3** the protonation as a model reaction of electrophilic addition was studied by the MNDO calculations method. The total energy of the system hydrocarbon-proton was estimated as a function of the center of propellane C-C bond...H^+ distance (Fig. 1) under the complete optimization of system geometry. The protonation of **1** with the 1-adamantylcation formation is accompanied by an intense decrease of the total system energy and decreasing of C-C...H^+ distances. On the contrary, the approach of H^+ to the C-C bond of **2** at a distance within 2.5Å gives only an insignificant decrease of the total system energy and even energy increase at shorter distances. According to the character of the E/C-C...H^+ relationship, the compound **3** occupies interim position between compounds **1** and **2**. The total system energy remains almost constant up to 3.5Å and decreases at shorter distances.

These findings are in good agreement with experimental results on the reactions of compounds **1-3** with protic acids. Propellane **1** adds acetic acid and phenol at low temperature without catalyst.[17] 1,5-Dehydrobicyclo[3.3.1]nonane (**3**) according to[18] adds acetic acid only under prolonged reflux. 3,6-Dehydrohomoadamantane (**2**)[19] exhibits kinetic stability exceptional for propellanes in the presence of protic acids and does not change under heating with mineral acids up to 50% concentration. This considerable difference in hydrocarbons **1-3** as well as other propellanes reactivity is worthy of a separate study and is beyond the scope of the present communication. It could certainly be affirmed that the electrophilic addition to **2** seemed to be the least probable in the series of hydrocarbons **1-3** studied.

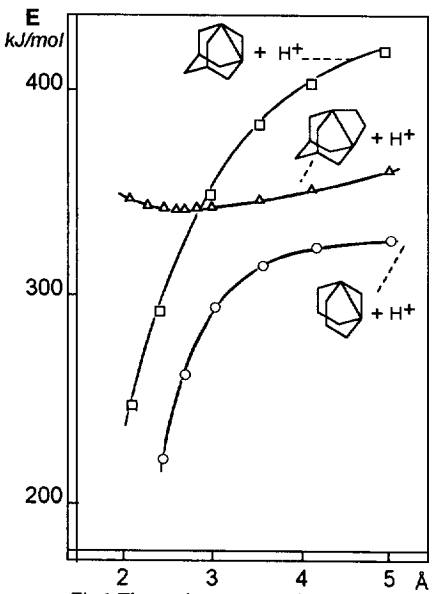


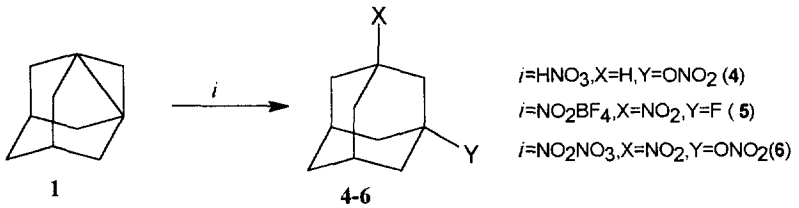
Fig.1 The total energy as a function of the C-C bond...H^+ distance.

The reactions of **1-3** with 100% nitric acid and nitronium reagents were studied in different reaction media CH_3CN, Ac_2O, EtOAc, MeOAc, and CH_2Cl_2.

Reactivity. As it was expected from the calculations described above and literature data the only reaction pathway of **1** with 100% nitric acid, nitroniun tetrafluoroborate and nitronium nitrate is the electrophilic addition to the strained C-C bond with the formation of 1-nitroxyadamantane (**4**), 1-fluoro-3-nitroadamantane (**5**) and 1-nitroxy-3-nitroadamantane (**6**)

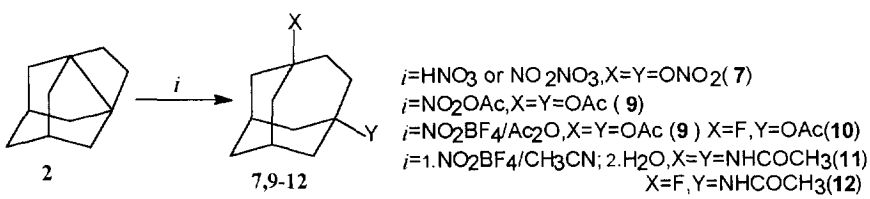
correspondingly (SCHEME 2). The low yield (37%) of nitrofluoride **5** is caused by the side formation of 1-fluoroadamantane and polymeric tar.

SCHEME 2



Fundamental differences between hydrocarbons **2** and **1** become apparent in the reaction with 100% nitric acid (SCHEME 3), 3,6-dinitroxyhomoadamantane (**7**) was formed as the only reaction product in a high yield. This compound was described earlier[20] as one of the products of homoadamantane dinitroxylation with nitric acid. We have found the compound **7** is not to be the product of consecutive addition of HNO_3 to the C^3-C^6 bond of compound **2** and subsequent nitroxylation of 3-nitroxyhomoadamantane (**8**) on the C^6-H bond because compound **8** was stable under dinitroxylation conditions of compound **2**. Thus, the formation of **7** cannot be explained by a traditional concept of the propellane C-C bond nucleophilic reactivity as in the case of **1**. The formation of **7**, at least formally, can be attributed to the oxidative transformation with nitronium nitrate (concentration of NO_2NO_3 in 100% nitric acid is high enough[21]), being an oxidant. To support this assumption, we have studied the reaction of pure NO_2NO_3. Compound **7** was formed under the

SCHEME 3

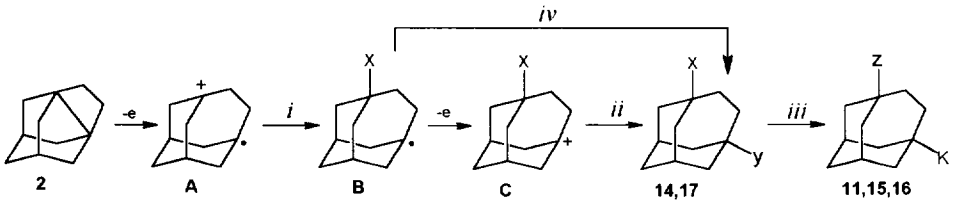


same conditions in a high yield, simultaneously the evolution of nitrogen oxides was observed. In the same way the reaction of **2** with nitronium acetate proceeds with the formation of diacetate **9**. As in the previous case the formation of **9** is not the result of the electrophilic addition of nitronium acetate to the C^3-C^6 bond of **2** and the substitution of NO_2 group for OAc. 3-Nitro-6-acetoxyhomoadamantane (**13**)[22] was found to be stable under the reaction conditions. The result of the compound **2** interaction with nitronium tetrafluoroborate is considerably dependent on the nucleophilicity of a solvent and the nucleophilic part of the reagent participation. The formation of fluoroderivatives was usually observed. Compound **2** gave diacetate **9** and fluoroacetate **10** with NO_2BF_4 in acetic anhydride and diacetamide **11** and fluoroacetamide **12** with NO_2BF_4 in CH_3CN. The ratios of **9**:**10** and **11**:**12** were dependent on the relative quantities of the reagent and

nucleophilic solvent used. Under a substantial excess of Ac_2O and CH_3CN **9** and **11** were the main reaction products isolated in a high preparative yields.

Thus, the oxidative addition of nucleophilic species to the strained C-C bond of **2** with a consecutive formation of carbocationic centers at 3 and 6 positions of the homoadamantane nucleus is characteristic of the nitronium reagents addition. The oxidative nature of the transformation was confirmed by a separate study of the electrooxidation of **2** in CH_3CN in the presence of NH_4BF_4 yielding the diacetamide **11** as the only reaction product. The general concept of the transformations may be depicted by SCHEME 4 which is quite close to that proposed[23] for the anodic oxidation of the alkane C-H bonds. The only difference consists in the absence of a leaving group (H^+) which in our case is represented by a carbon atom of C^3-C^6 bond being cleaved with the cation radical **A** formation. The subsequent oxidation of the radical **B** gave the cation

SCHEME 4



i=*ii*= CH_3CN,BF_4^-, *iii*=H_2O, X=Y=(N=CCH 3)$^+$$(BF_4^-)$, K=Z=NHCOCH 3 (**11**)
i=*ii*=F^-, X=Y=F (**14**)
i=F^-, *iii*= NO_2BF_4, *iv*=NO_2, X=Z=F, Y=ONO, K=ONO 2 (**15**)
i=F^-, *iii*= NO_2BF_4, *iv*=NO_2, X=Z=F, Y=ONO, K=NO 2 (**16**)
i=F^-, *iv*=NO_2, X=F, Y=ONO (**17**)

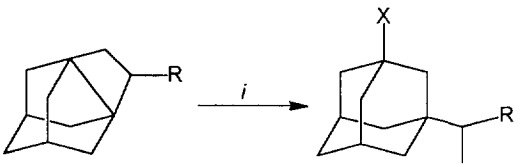
C and the reaction product after its interaction with nucleophile.

The reaction of compound **2** with NO_2BF_4 in low- or nonnucleophilic media (MeOAc, EtOAc or CH_2Cl_2) proceeds in a somewhat different way. With a 2.5 mole excess of the reagent in MeOAc or EtOAc **2** mainly gave 3,6-difluorohomoadamantane (**14**). This confirms the assumption of the consecutive formation of carbocationic centers at C^3 and C^6 and their interaction with BF_4^- as a nucleophile. A simultaneous formation of substantial quantities of 3-fluoro-6-nitroxyhomoadamantane (**15**) and small quantities of 3-fluoro-6-nitrohomoadamantane (**16**) was unexpected. When 1.5 excess of NO_2BF_4 has been used, a relative quantity of **16** has increased. The formation of **15** and **16** may be explained by the recombination of the radical **B** into compound **16** and nitritoester **17** and its subsequent rearrangement into **16**. At the same time **17** can be oxidized to nitroxyderivative **15** by the excess of NO_2BF_4. We have found that 3-homoadamantylnitrite with NO_2BF_4 gave 3-nitroxyhomoadamantane (**8**) under the same reaction conditions. The rearrangement of 1-adamantylnitrite into nitrocompound was studied earlier.[6] The formation of nitrite **17** on the addition of NO_2^+ as an O-electrophile[24] seems to be unlikely if the resultant product of the interaction of **1** with NO_2BF_4 is

taken into consideration. Pure compounds **14-16** were found to be stable under reaction conditions, this excludes their interconvertions in the course of the reaction.

The reaction of **2** with NO_2BF_4 in CH_2Cl_2 (SCHEME 5) is heterogeneous and is accompanied by polymerization which decreases the yield of an isolable material. 1-Nitroxy-3-fluoromethyladamantane (**18**) was isolated in 24% yield as the only product whose origin can be explained by the rearrangement of 3-homoadamantyl into 1-adamantylmethyl cation. Such rearrangement is typical of 3-homoadamantane

SCHEME 5



R=H (**2**)
R=CH_3 (**19**)

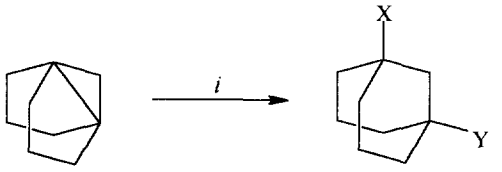
R=H (**18**)
R=CH_3 (**20-24**)

i=NO_2BF_4/CH_2Cl_2,X=ONO_2,Y=F (**18**)
i=HNO_3,X=Y=ONO_2 (**20**)
i=NO_2OAc,X=Y=OAc (**21**)
i=NO_2BF_4,X=Y=F (**22**)
X=F,Y=ONO_2 (**23**)
X=F,Y=NO_2 (**24**)

derivatives.[25] 1-Fluoro-3-fluoromethyladamantane was formed only in trace quantities and identified by GC-MS data. 4-Methyl-3,6-dehydrohomoadamantane (**19**) underwent (SCHEME 5) the rearrangement into the adamantane structure on the interaction with nitronium reagents in media of any nucleophilicity, possibly, because of an 1-adamantyl-1-ethen-1-yl cation higher stability. In general, the formation of **20-24** corresponded to the oxidative addition pathway proposed for the transformations of **2**.

All the data on the reactivity of **2** and **19** demonstrated that the oxidation of the C^3-C^6 bond in the 3,6-dehydrohomoadamantane structure was caused by its stability towards electrophilic reagents. This excludes the competitive electrophilic addition, characteristic to compound **1** reactivity with nitronium reagents. In this respect the reactivity of hydrocarbon **3** is of special interest. The study of the reactivity of **3** towards nitronium reagents was performed under the same conditions as in the case of compound **2**. The only direction of its interaction with 100% nitric acid and nitronium reagents was the oxidative addition to the C^1-C^5 bond (SCHEME 6).

SCHEME 6



3

25-29

i=HNO_3,X=Y=ONO_2 (**25**)
i=NO_2OAc,X=Y=OAc (**26**)
i=NO_2BF_4,X=Y=F (**27**)
X=F,Y=ONO_2 (**28**)
X=F,Y=NO_2 (**29**)

1,5-Dinitroxybicyclo[3.3.1]nonane (**25**) was isolated in a high yield under the treatment of **3** with 100% HNO_3 and 1,5-diacetoxybicyclo[3.3.1]nonane (**26**) with NO_2OAc. Compound **3** gave 1,5-difluorobicyclo[3.3.1]nonane (**27**), 1-fluoro-5-nitroxybicyclo[3.3.1]nonane (**28**), and less than 3% of 1-fluoro-

5-nitrobicyclo[3.3.1]nonane (**29**) with NO_2/EtOAc. The results demonstrate low reactivity of **3** in electrophilic transformations and faster oxidative processes on the propellanic C-C bond.

CONCLUSIONS

The transformations of propellanes **1-3** and **19** under the treatment with 100% nitric acid and nitronium salts displayed the substrate structure to be decisive in determining the course of the reaction. In the case of **1** the electrophilic addition according to the *backside* Ad_E scheme, usual for propellanes, took place. Under the same conditions propellanes **2,3** and **19** formed the products with the two nucleophilic groups added. This cannot be explained by the traditional concept of the propellane hydrocarbons reactivity. It was demonstrated that the C-C bond of hydrocarbons stable in electrophilic media could be oxidized by nitronium oxidizers. The mechanisms of these transformations certainly need a more detailed study, but it is clear that the results have revealed new aspects of the alkane C-C bond reactivity, *backside* oxidative addition Ad_{Ox}.

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EXPERIMENTAL SECTION

All syntheses were carried out under argon in anhydrous solvents distilled under argon prior to use. Propellanes **1** and **3** were obtained under the treatment of K/Na alloy in ether from 1,3-dibromoadamantane and 1,5-dibromobicyclo[3.3.1]nonane, respectively. 3,6-Dehydrohomoadamantane (**2**) was obtained according to [19]. 4-Methyl-3,6-dehydrohomoadamantane (**19**) by photocyclization of 3-methylene-7-ethylidenobicyclo[3.3.1]nonane.[26] Nitronium tetrafluoroborate was prepared from HNO_3, HF and BF_3 in nitromethane. NO_2NO_3 was obtained from HNO_3 and P_2O_5, distilled in O_3 flow and recrystallized twice from CH_2Cl_2 at -30°C. Silica 40/100 for chromatography was obtained from Lachema. NMR spectra were recorded in $CDCl_3$ solutions on a Varian Models VXR-300 and Gemini-200 (TMS as internal standard for PMR and NMR^{13}C and $CFCl_3$ - for NMR^{19}F); IR (cm^{-1}) - on Specord IR-75 in $CHCl_3$ solutions. GC-MS data were obtained on Hewlett-Packard 5890-II with MSD 5970B. Melting points are uncorrected.

1. Reaction of 1,3-Dehydroadamantane (1) with:

a) 100% HNO_3. Mixture of 4 ml 100% HNO_3 and 2 ml of CH_2Cl_2 was added to a solution of **1** (500mg) in 5 ml of CH_2Cl_2 at -10°C, kept 10 min at this temperature and poured on ice. The mixture was extracted by CH_2Cl_2 (3x5 ml), the combined extracts were washed with water, Na_2CO_3 solution, brine, dried over Na_2SO_4 and solvent was distilled off. The residue was **1-adamantylnitrate (4)**, yield 680mg (93%).

b) NO_2NO_3. Solution of **1** (500 mg) in 7 ml CH_2Cl_2 was added dropwise to a solution of 1g N_2O_5 in 10 ml CH_2Cl_2 at -20°C, kept 1 h at that temperature and worked as in 1a. The mixture was separated by column chromatography (hexane-ether 3:1). **1-Adamantylnitrate (4)** (50 mg, 6.8%) was isolated as first fraction along with **1-nitroxy-3-nitroadamantane (6)** yield 640 mg (80%), m.p. 78-79°C. PMR:1.68 (AB-system, 4H), 1.72 (bs, 2H), 2.20 (AB-system, 4H), 2.57 (bs, 2H), 2.64 (s, 2H). NMR^{13}C: 31.14, 34.37, 38.57, 39.98, 42.88, 85.84, 88.62. IR: 2850-2950, 1620, 1537, 1357, 1280, 860. Found: C 49.81; H 5.93; N 11.19. Calc. for $C_{10}H_{14}N_2O_5$: C 49.58; H 5.82; N 11.56.

c) NO_2BF_4/CH_2Cl_2. The solution of 1 (600 mg) in 8 ml CH_2Cl_2 at 0°C was added to a stirred suspension of NO_2BF_4 (690 mg) in 8 ml CH_2Cl_2, kept under stirring for 10 min, poured in excess water and worked up as in 1a. The mixture was separated by column chromatography (hexane-ether 9:1). **1-Fluoroadamantane** (83 mg, 12%) was isolated as a first fraction along with **1-fluoro-3-nitroadamantane (5)**, yield 308 mg (37%), m.p. 157-159°C. PMR: 1.62 (bs,2H), 1.91-1.94 (m,4H), 2.17 (m,4H), 2.39 (d,5.2 Hz, 2H), 2.53 (bs, 2H). $NMR^{13}C$: 31.17 (d,10 Hz), 34.10, 39.73, 41.19 (d,18 Hz), 45.64 (d,22.6 Hz), 86.11 (d, 11.3 Hz), 92.02 (d,187.8). IR: 2840-3000, 1534, 1365. $NMR^{19}F$: -135.5. MS: 153 (M-NO_2, 100%), 133 (18%), 97 (30%), 77 (15%), 44 (20%). Found: C 60.40; H 7.31; N 6.87; F 9.31. Calc. for $C_{10}H_{14}NO_2F$: C 60.29; H 7.08; N 7.03; F 9.54.

2. Reaction of **3,6-Dehydrohomoadamantane (2)** with:

a) 100% HNO_3. From 1 g of **2** and 8 ml 100% HNO_3 according to procedure 1a **3,6-dinitroxy-homoadamantane (7)** was obtained, identical to an authentic sample[20] according spectral data. Yield 1.65 g (90%).

b) NO_2NO_3/CH_2Cl_2. From 1 g of **2** and 550 mg of NO_2NO_3 according to procedure 1b at -10°C 845 mg (92%) of compound (**7**) was obtained.

c) NO_2OAc . The mixture of 5 ml CH_2Cl_2, 4 ml Ac_2O, 0.4 ml HNO_3 and 0.04 ml H_2SO_4 was kept 10 min at 25°C, than cooled to 0°C. To the mixture the solution of 300 mg of **2** in 5 ml CH_2Cl_2 was added dropwise, kept 10 min at 0°C and diluted by excess water up as in 1a. The mixture was separated by column chromatography (hexane-ether 4:1), **3,6-diacetoxyhomoadamantane (9)** was obtained, yield 485 mg (91%), m.p. 88-90°C (hexane). PMR: 1.45 (bs,2H), 1.82 (s,6H), 2.12 (s,4H), 1.90-2.13 (m,10H). $NMR^{13}C$: 22.59, 28.87, 33.23, 34.89, 42.58, 84.24, 170.06. IR: 2930-3000, 1730. MS: 206 (M-HOAc, 20%), 164 (45%), 146 (65%), 106 (57%), 91 (30%), 43 (100%). Found: C 67.29; H 8.35. Calc. for $C_{15}H_{22}O_4$: C 67.65; H 8.32.

d) NO_2BF_4/Ac_2O. 1.5 ml of Ac_2O and a solution of **2** (650 mg) in 5 ml CH_2Cl_2 was added to a stirred suspension of 0.7 g NO_2BF_4 in 10 ml CH_2Cl_2 at 0°C, the mixture was stirred for 1 hour and diluted by excess water. After workup according to procedure 2a the mixture was separated by column chromatography (hexane-ether 5:1). As a first fraction **3-fluoro-6-acetoxyhomoadamantane (10)** was isolated, yield 150 mg (15 %), PMR: 1.55 (bs,2H), 1.80 (s,3H), 2.05-2.25 (m,8H), 2.45-2.60 (m,4H), 2.50 (bs, 2H). $NMR^{13}C$: 22.32, 27.95 (d,11.3 Hz), 31.65 (d, 24.3 Hz), 31.91 (d,15.2 Hz), 33.50, 41.50 (d,20.9 Hz), 42.61, 84.45, 93.65 (d, 169.1 Hz), 170.34. $NMR^{19}F$: -110.8. IR: 2930-3000, 1730. MS: 166 (M-HOAc, 100%), 106 (40 %), 95 (30%), 70 (37%), 43 (93%). Found: C 69.11; H 8.29; F 8.20. Calc. for $C_{13}H_{19}O_2F$: C 69.00; H 8.46; F 8.39. The main fraction contains compound **9**. Yield 760 mg (65%).

e) NO_2BF_4/CH_3CN . 187 mg of **2** in 5 ml CH_3CN was added to a stirred solution of 420 mg NO_2BF_4 in 10 ml CH_3CN, kept 1 hour at 25°C, diluted by excess water, CH_3CN was distilled off in vacuum. The residue was extracted by $CHCl_3$ (3x5 ml) the extract was washed by water, dried over Na_2SO_4 and $CHCl_3$ was distilled off. The mixture was filtered through silica (ether-methanol 10:1). **3,6-Diacetaminohomoadamantane (11)** was obtained, yield 300 mg (90%), m.p. 232-234°C ($CHCl_3$). PMR: 1.47 (m,2H), 1.75-1.89 (m,4H), 1.90-2.05 (m,10H), 2.07 (s,6H), 5.12 (bs,2H). $NMR^{13}C$: 25.05, 28.53, 35.41, 36.38, 43.16, 56.61, 169.35. IR: 5415, 3010, 2710-3000, 1660, 1505. Found: C 68.17; H 8.92; N 10.66. Calc. for $C_{15}H_{24}O_2N_2$: C 68.15; H 9.15; N 10.59.

f) $NO_2BF_4/CH_3CN/CH_2Cl_2$ From 420 mg NO_2BF_4 in 14 ml CH_2Cl_2 and 292 mg **2** in 7 ml CH_2Cl_2 according to procedure 2e **3-fluoro-6-acetaminohomoadamantane (12)** was obtained, yield 439 mg (55%), m.p. 113-114°C. PMR: 1.50 (m,2H), 1.70-1.83 (m,4H), 1.93 (s,3H), 1.80-2.05 (m,10H), 5.10 (bs, 1H). $NMR^{13}C$: 22.67, 26.53 (d,11.5 Hz), 31.19 (d,16.2 Hz), 32.70 (d, 2 Hz), 34.27 (d, 26.2 Hz), 40.77,41.72 (d,20.4 Hz), 54.09, 94.14 (d, 168.8 Hz), 167.03. $NMR^{19}F$:-110.5. IR: 3420, 3000, 2800-2990, 1665, 1506. Found: C 69.39; H 8.75; N 6.51; F 8.42. Calc. for $C_{13}H_{20}OFN$: C 69.30; H 8.95; N 6.22; F 8.43. The second fraction contained compound **11**, yield 300 mg (40%).

g) NO_2BF_4/EtOAc. 300 mg of **2** in 15 ml EtOAc was added to a stirred solution of 680 mg NO_2BF_4 in 70 ml EtOAc, kept under stirring 1 hour and worked up with excess water. Water layer was extracted by EtOAc (2x20 ml). Organic layer and extracts were combined, filtered through silica and evaporated. The residue was separated by column chromatography (hexane-ether 10:1) and the compounds **14-16** were obtained. **3.6-Difluorohomoadamantane (14)** yield 120 mg, (31 %), m.p.119-120°C (hexane). PMR: 1.70 (bs,2H), 2.00-2.25 (m,8H), 2.50-2.75 (m,4H), 2.52 (bs,2H). $NMR^{13}C$: 27.61 (t,11.5 Hz), 31.73 (m), 32.52 (t,2 Hz), 41.51 (d, 20.9 Hz), 93.86 (d,169.8 Hz). $NMR^{19}F$: -112.03. IR: 2950-2800. MS: 186 (M,60%), 113 (100 %), 107 (96%), 70 (68%), 39 (38%). Found: C 70.70; H 8.76; F 20.15. Calc. for $C_{11}H_{16}F_2$: C 70.94; H 8.66; F 20.40. **3-Fluoro-6-nitroxyhomoadamantane (15),** yield 125 mg, 26%), m.p. 77-78°C (hexane). PMR: 1.59 (m,2H), 1.92-2.09 (m,4H), 2.22-2.42 (m,10H). $NMR^{13}C$: 27.12 (d,11.6 Hz), 28.70

(d,15.6 Hz), 32.34, 32.63 (d,24.8 Hz), 38.89, 41.20 (d,21.1 Hz), 91.73, 93.50 (d,169.6 Hz). NMR^{19}F: -111.7. IR: 2890-3000, 1610, 1250, 850. Found: C 57.69; H 7.29; N 5.88; F 7.97. Calc. for $C_{11}H_{16}NO_3F$: C 57.63; H 7.03; N 6.11; F 8.29. **3-Fluoro-6-nitrohomoadamantane (16)** (35 mg, 8%), m.p. 171-173°C (hexane). PMR: 1.55 (m,2H), 1.90-2.10 (m,4H), 2.17-2.39 (m,10H). NMR^{13}C: 26.77 (d,11.4 Hz), 31.74 (d,16.5 Hz), 32.01, 33.59 (d,28.2 Hz), 38.95, 41.38 (d,21.1 Hz), 88.03, 92.89 (d,170.4 Hz). NMR^{19}F: -114.61. IR: 2900-3000, 1540, 1370. MS: 167 (M-NO_2, 100%), 147 (40%), 105 (41%), 91 (38%), 41 (43%). Found: C 61.85; H 7.71; N 6.32; F 8.81. Calc. for $C_{11}H_{16}NO_2F$: C 61.96; H 7.56; N 6.57; F 8.91.

h) NO_2BF_4/CH_2Cl_2. 300 mg of **2** in 15 ml CH_2Cl_2 was added to a stirred suspension of NO_2BF_4 (650 mg) in 30 ml CH_2Cl_2. The mixture was stirred for 5 hours and worked up as in procedure 1c. By column chromatography (hexane-ether 10:1) **1-nitroxy-3-fluoromethyladamantane (18)** was isolated, yield 110 mg (24%). PMR: 1.55 (m,4H), 1.67 (m,2H), 1.97 (bs,2H), 2.10-2.12 (m,4H), 2.30-2.40 (m,2H), 4.05 (d, 47.8Hz, 2H). NMR^{13}C: 30.85, 35.79, 37.27 (d, 4.3Hz), 38.97 (d, 18Hz), 39.72, 40.94 (d, 4.7Hz), 90.13, 91.43 (d, 173.3Hz). NMR^{19}F: -231 (t, 48 Hz). IR: 2970-2880, 1615, 1270, 850. Found: C 57.40; H 7.05; N 5.93; F 8.04. Calc. for $C_{11}H_{16}NO_3F$: C 57.63; H 7.03; N 6.11; F 8.29.

3. Electrooxidation of 2 in CH_3CN. Mixture 174 mg of **2**, 75 ml of CH_3CN and 200 mg of NH_2BF_4 were placed into glass cell with platinum electrodes and subjected to direct current at 2.5 V anode potential during 6 hour. The reaction mixture was diluted by excess water and worked as in procedure 2e. The compound **11** was obtained in 87% yield (260 mg).

4. Reaction of **4-methyl-3,6-dehydrohomoadamantane (19)** with:

a) 100 % HNO_3. From 130 mg of **19**, 1.3 ml 100% HNO_3 in 2 ml CH_2Cl_2 at 0°C according to procedure 1a and column chromatography purification (hexane-ether 5:1) **1-nitroxy-3-(1-nitroxyethyl)adamantane (20)** was obtained. Yield 172 mg (75%). PMR: 1.27 (d, 6.5Hz,3H), 1.62 (m,6H), 1.95 (m,2H), 2.09 (m,4H), 2.35 (m,2H), 4.70 (q, 6.5Hz,1H). NMR^{13}C: 10.83, 28.48, 33.25, 34.60, 34.72, 37.24, 38.22, 38.65, 84.20, 87.50. IR: 2930-2850, 1620, 1260, 850. Found: C 50.41; H 6.42; N 9.55. Calc. for $C_{12}H_{18}N_2O_6$: C 50.35; H 6.34; N 9.79.

b) NO_2BF_4/Ac_2O. From 155 mg of **19**, 393 mg NO_2BF_4 in 5 ml Ac_2O and 5 ml CH_2Cl_2 according to procedure 2d and column chromatography purification (hexane-ether 5:1) 195 mg (73%) **1-acetoxy-3-(1-acetoxyethyl)adamantane (21)** was obtained. PMR: 1.05 (d, 6.6Hz, 3H), 1.35-1.52 (m, 6H), 1.81 (m, 2H), 1.91 (s,3H), 1.98 (s, 3H), 1.95-2.05 (m, 4H), 2.17 (m,2H), 4.54 (q, 6.6 Hz, 1H). NMR^{13}C: 11.77, 19.23, 20.67, 28.42, 33.78, 34.87, 35.07, 37.79, 38.87, 39.70, 74.69, 78.58, 168.17, 168.67. IR: 2980-2850, 1720. Found: C 68.56; H 8.31. Calc. for $C_{16}H_{24}O_4$: C 68.54; H 8.63.

c) NO_2BF_4/EtOAc. From 385 mg of **19**, 740 mg NO_2BF_4 in 85 ml EtOAc according with procedure 2g and column chromatography separation compounds **22-24** were obtained. **1-Fluoro-3-(1-fluoroethyl)adamantane (22),** yield 162 mg (34%). PMR: 1.12 (dd, 23 Hz, 6.5 Hz, 3H), 1.32- 1.65 (m, 8H), 1.68-1.87 (m, 4H), 2.25 (m, 2H), 4.02 (dd, 6.5Hz, 48Hz, 1H). NMR^{13}C: 14.98 (d, 24.1Hz), 31.44 (d, 9.6Hz), 35.96, 36.54-36.65 (m), 42.01 (dd, 9.4Hz, 19.5Hz), 42.71, 43.06, 43.11 (dd, 4.4Hz, 18.5Hz), 93.01 (d, 183,7Hz), 96.42 (d, 171.3Hz). NMR^{19}F: -132.19, -185.41. IR: 2980-2800. MS: 200 (M, 5%), 153 (100%), 133 (15%), 97 (18%). Found: C 72.16; H 9.10; F 18.57. Calc. for $C_{12}H_{18}F_2$: C 71.97; H 9.06; F 18.97. **1-Nitroxy-3-(1-fluoroethyl)adamantane (23)** , yield 52 mg (9%). PMR: 1.12 (dd, 23Hz, 6.5Hz, 3H), 1.45-1.80 (m, 6H), 1.87 (m, 2H), 2.05 (m,4H), 2.32 (m,2H), 4.05 (dd, 6.5Hz, 48 Hz, 1H). NMR^{13}C: 14.96 (d, 24 Hz), 31.06, 36.00, 36.43 (d, 3.8 Hz), 36.74 (d, 4.3 Hz), 39.94, 40.31 (d, 4.5 Hz), 40.96 (d, 10Hz), 41.48 (d, 19.4Hz), 90.53, 96.33 (d, 171.9Hz). NMR^{19}F: -185.70. IR: 2950-2830, 1620, 1270, 850. Found: C 59.45; H 7.28; N 5.89; F 7.73. Calc. for $C_{12}H_{18}NO_3F$: C 59.25; H 7.46; N 5.76; F 7.81. **1-Nitro-3-(1-fluoroethyl)adamantane (24),** yield 134 mg (25%). PMR: 1.12 (dd, 23 Hz, 6.5 Hz, 3H), 1.43-1.75 (m, 6H), 1.85 (m, 2H), 2.03 (m, 4H), 2.30 (m,2H), 4.05 (dd, 6.5Hz, 48 Hz, 1H). NMR^{13}C: 14.87 (d, 24Hz), 30.00, 35.64, 36.05 (d, 3.8Hz), 36.48 (d, 4.3Hz), 41.02, 41.10-41.40 (m), 41.83 (d, 4.6Hz), 85.55, 96.26 (d, 171.9Hz). NMR^{19}F: -186.04. IR: 3000-2890, 1530, 1370. Found: C 63.54; H 8.03; N 5.91; F 8.17. Calc. for $C_{12}H_{18}NO_2F$: C 63.42; H 7.98; N 6.16; F 8.36.

5. Reaction of **1,5-dehydrobicyclo[3.3.1]nonane (3)** with:

a) 100% HNO_3. From 100 mg of **3** in 3 ml of CH_2Cl_2 and 0.7 ml HNO_3 according to procedure 1a **1,5-dinitroxybicyclo[3.3.1]nonane (25)** was obtained, yield 164 mg (83%), identical by spectral data to the authentic sample.[20]

b) NO_2BF_4/Ac_2O. From 132 mg of **3** according to procedure 2d **1,5-diacetoxybicyclo[3.3.1]nonane (26)** was obtained, yield 217 mg (85%). PMR: 1.78 (m, 8H), 1.95 (s,6H), 2.12 (s,2H), 2.33-2.42 (m,4H). NMR^{13}C: 21.33, 22.87, 34.84, 44.85, 83.83, 170.25. IR: 3000-2870, 1720. Found: C 64.90; H 8.45. Calc. for $C_{13}H_{20}O_4$: C 64.98; H 8.39.

c) NO_2BF_4/EtOAc. From 220 mg of **3** according to procedure 2g and column chromatography separation compounds **27-29** were obtained. **1,5-Difluorobicyclo[3.3.1]nonane (27),** 164 mg (57%). PMR: 1.60-1.69 (m, 8H), 1.75-1.87 (m, 6H). NMR^{13}C: 20.32 (t, 13.2Hz), 35.76-36.20 (m), 47.78 (t, 17.8Hz), 96.70 (dd, 12.7Hz, 178.6Hz). NMR^{19}F: -128.37. MS: 160 (M, 3%), 117 (100%), 97 (10%), 72 (27%). IR: 3000-2840. Found: C 67.49; H 8.99; F 23.53. Calc. for $C_9H_{14}F_2$: C 67.47; H 8.81; F 23.72. **1-Fluoro-5-nitroxybicyclo[3.3.1]nonane (28)**, yield 44 mg, (12%). PMR: 1.72-2.03 (m). NMR^{13}C: 20.8 (d, 12.4Hz), 33.20 (d, 1.6Hz), 36.00 (d, 22.2Hz), 44.28 (d, 20.5Hz), 93.4 (d, 12.4Hz), 95.70 (d, 178.0Hz). IR: 3000-2850, 1620, 1270, 850. Found: C 53.38; H 6.81; N 6.98; F 9.22. Calc. for $C_9H_{14}NO_3F$: C 53.19; H 6.94; N 6.89; F 9.35. **1-Fluoro-5-nitrobicyclo[3.3.1]nonane (29)**, yield 8 mg (2%). IR: 3000-2820, 1530, 1370. MS: 141 (M-NO_2, 40%), 121 (100%), 99 (35%), 93 (83%), 79 (80%), 67 (31%), 41 (43%).

6. 3-Nitro-6-acetoxyhomoadamantane (13) was obtained in 95% yield from **16** under the treatment by excess of NO_2BF_4 in Ac_2O at room temperature during 48 h . PMR: 1.55 (m,2H), 1.92 (s,3H), 2.10 (m,2H), 2.12-2.45 (m, 12H). NMR^{13}C: 22.83, 28.76, 33.97, 34.42, 35.36, 41.16, 42.66, 83.37, 90.21, 170.33. IR: 3000-2900, 1720, 1535, 1370. MS: 207 (M-NO_2, 12%), 193 (M-HOAc, 23%), 147 (100%), 105 (43%), 91 (51%), 43 (88%). Found: C 61.69; H 7.59; N 5.23. Calc. for $C_{13}H_{19}NO_4$: C 61.64; H 7.56; N 5.53.

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