Hydrocarbon Activation with Cerium(IV) Ammonium Nitrate: Free Radical versus Oxidative Pathways

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The reactivity of propellane C–C bonds towards cerium(IV) ammonium nitrate (CAN) was studied utilizing photochemical initiation in acetonitrile. Synthetic as well as computational (B3LYP/6-311+G** and MP2/6-31G*) data strongly suggest that the activation of the C–C bonds in cyclopropane and cyclobutane derivatives involves NO_3 radical attack on the hydrocarbon ring and does not proceed through single electron transfer. The product structures are not consistent with the intermediate formation of propellane radical cations. These propellane systems could be generated independently by oxidation with charged electrophiles, by anodic oxidation, and through photo-oxidation with 1,2,4,5-tetracyanobenzene; the observed chemical behavior of radical cations is clearly different.

Introduction

Cerium(IV) ammonium nitrate (CAN) is widely employed in organic synthesis for the oxidation of olefins,[1] enol ethers,[2] alcohols,[3] sulfides,[4] oxidative fragmentation of diols,[5] and many other transformations. However, the oxidative power of CAN (E_{red} = 1.27 V vs. SCE) is too low to oxidize hydrocarbons generally. The oxidizer can only be applied to electron-rich substrates such as *p*-methoxyaryl derivatives,[6] 1,2-diarylethanes,[7] benzylcyclopropanes[8] as well as naphthyl- and anthranylcyclopropanes.[9] On the other hand, CAN produces unstable and thus highly reactive nitrate radicals ($NO_3^{\bullet}$) upon photochemical initiation.[10] These radicals exhibit high electrophilicity combined with a higher oxidation potential (E_{red} = 2.0 V vs. SCE in acetonitrile).[11] As a consequence, NO_3 radicals do react with saturated hydrocarbons with unexpectedly high selectivities, presumably due to substantial polarization of the transition structures for C−H hydrogen abstraction. For instance, the selectivity of tertiary over secondary adamantane nitroxylation is 1.00:0.07.[12] Similar selectivities (about 95%) were observed for the low-temperature Kyodai nitration of adamantane[13] in the NO_2/O_3 system, which also produces $NO_3^{\bullet}$ as the reactive intermediate. It was also shown that alkyl aromatics form side-chain nitroxy derivatives in the presence of NO_3 radicals.[14] Two different mechanisms, one oxidative through single electron transfer (SET) followed by α-proton loss from the intermediate radical cation[15] and one by α-hydrogen radical abstraction,[16] were proposed for this reaction. In the absence of α-aromatic hydrogen atoms in the substrate, NO_3 radicals are able to cleave saturated C−C bonds in the β-position relative to the aromatic fragment. This was found for 2,3-dimethyl-2,3-diphenylbutane,[14b] which forms 1,2-dinitroxy-2-phenylpropane and some other fragmentation products.

Arylcyclopropanes are quite suitable model hydrocarbons for studying C−C bond activation mechanisms.[9,17] Equations (1) and (2) represent two possible pathways for the reactions of these compounds with NO_3 radicals: Oxidation [Equation (1)] by SET from the aromatic fragment to $NO_3^{\bullet}$, followed by C−C bond fragmentation and an S_R2 mechanism [Equation (2)], which involves direct attack of NO_3 on the cyclopropyl carbon atom. The structures of the products do not reveal details of the activation step as dinitroxy derivatives can be formed in both cases. Some evidence for SET involving aromatic radical cations was obtained from kinetic measurements of side-chain deprotonation in arylalkanes with NO_3 radicals.[15,16] As similar products were formed for arylcyclopropanes with CAN under photochemical[8] and thermal conditions,[9] the SET activation is usually favored in the literature.

The NO_3 radical is not as effective an SET oxidant as usually assumed. The electron affinity of $NO_3^{\bullet}$, computed for the $NO_3^{\bullet}/NO_3^-$ couple is only 90.0 and 94.8 kcal/mol at B3LYP and CCSD(T)/cc-pVTZ, respectively,[18] (experimentally 90.4 kcal/mol),[19] and is too low to oxidize aromatic hydrocarbons [Equation (1)]. Similarly, the nitrosonium cation NO^+ (electron affinity = 224.2 kcal/mol[20]) is known to be an effective SET oxidant only for some easily oxidizable aromatic compounds.[21] In contrast, cyclopropane ring opening by direct radical S_R2 attack on the carbon atom [Equation (2)], has a barrier of only 0.9 kcal/mol

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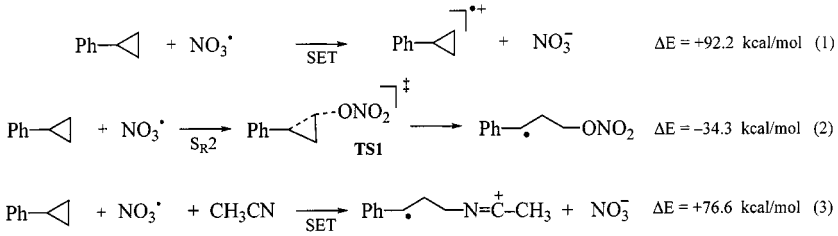


and is *exothermic* by −34.3 kcal/mol [for the geometry of the transition structure (**TS1**) see Figure 1]. The stabilization of the **TS1** by the phenyl substituent is comparable to that of alkyl groups: We located an analogous transition structure (**TS2**, Figure 1) for the addition of the NO_3 radical to dimethylcyclopropane (the barrier is 3.6 kcal/mol at the same level of theory).

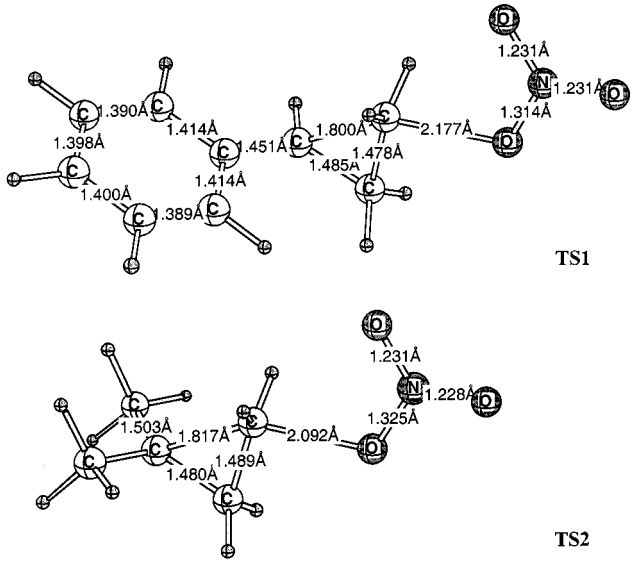


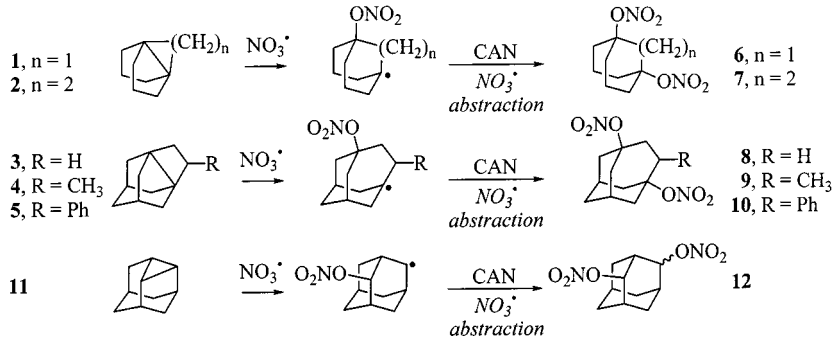
Figure 1. The transition structures for the $NO_3^{\bullet}$-initiated ring opening of phenylcyclopropane (**TS1**) and 1,1-dimethylcyclopropane (**TS2**) computed at B3LYP/6−31G*

This simple analysis of the thermochemistry of SET vs. radical pathways in the $NO_3^{\bullet}$/phenylcyclopropane system does not support SET activation [Equation (1)]. The computed gas phase endothermicity is reduced by solvation of the ions in the condensed state; an evaluation using the Rehm−Weller equation[22] shows a positive driving force for oxidation of alkylaromatics in acetonitrile.[16] This is mainly due to the low reorganization energy for the $NO_3^{\bullet}/NO_3^-$ couple[16] and to solvation of the radical cation by acetonitrile. This situation is supported by the finding that the inclusion of just one explicit acetonitrile solvent molecule in the evaluation of Equation (1) decreases the endothermicity for the SET by ca. 16 kcal/mol [Equation (3)].

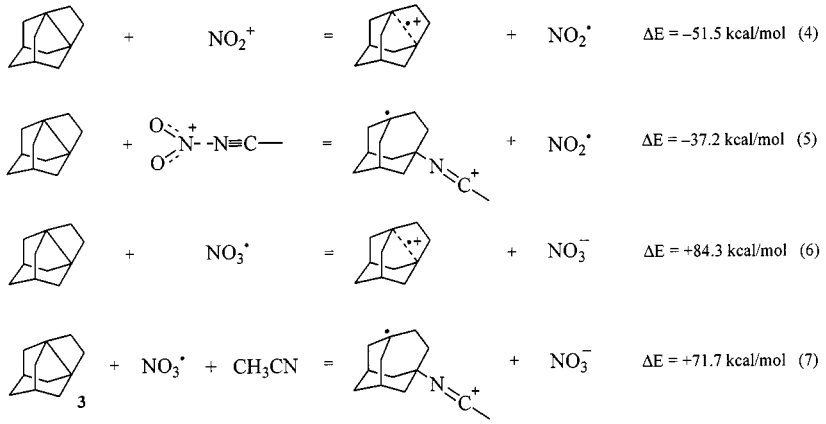
The present study addresses two key questions: (*i*) Can the NO_3 radical activate relatively strong σ_{C-C} bonds in structures not stabilized by aromatic groups and (ii) what is the role of SET vs. nonionic radical processes in σ_{C-C} bond activations with CAN? In answering these quetsions, we report on the reactions of CAN with propellanes, which have much higher oxidation potentials[23] than substituted aromatic compounds used in earlier studies. These model hydrocarbons allow us to vary the reactivity of the central σ_{C-C} bonds widely while avoiding side reactions. Propellanes were successfully used in our,[24] and other[25] groups for model studies on hydrocarbon activations with various electrophiles and radicals.

Results and Discussion

For the reasons discussed above we studied the reactivity of [3.3.1]propellane (**1**), [3.3.2]propellane (**2**), and some "bridged" propellanes based on the 3,6-dehydrohomoadamantane (**3**) framework, namely substituted propellanes **4** and **5**, with CAN (Scheme 1). The vertical ionization potentials of these hydrocarbons (I_v = 209.7 for **1**, 221.3 for **2**, and 216.5 kcal/mol for **3**)[23] as well as the oxidation potentials (2.42 and 2.31 V vs. SCE in acetonitrile for **2** and **3**[26]) are too high to be oxidized with $NO_3^{\bullet}$ (vide supra). Surprisingly, we found that upon photo-initiation in acetonitrile, CAN rapidly reacts with the C−C bonds of propellanes **1**−**5**. Dinitroxy derivatives (**6**−**10**, Scheme 1)[27] are formed in high preparative yields; these reactions only occur under photo-initiation.[28] Another cyclopropane-containing (nonpropellanic) hydrocarbon, 2,4-dehydroadamantane



Scheme 1. Reactions of propellanes **1**−**5** and 2,4-dehydroadamantane (**6**) with NO_3 radicals generated under photochemical conditions



(**11**), is also dinitroxylated efficiently under similar reaction conditions leading to a mixture of diastereomeric dinitroxy derivatives **12** in high yield. The reactive NO_3 radical formed through CAN homolysis is likely to attack the propellanic quaternary carbon atom directly and we suggest that the formation of *unrearranged* homoadamantane dinitroxy derivatives **9** and **10** convincingly shows that neither radical cations, nor carbocations form in the reactions of propellanes with $NO_3^\bullet$.

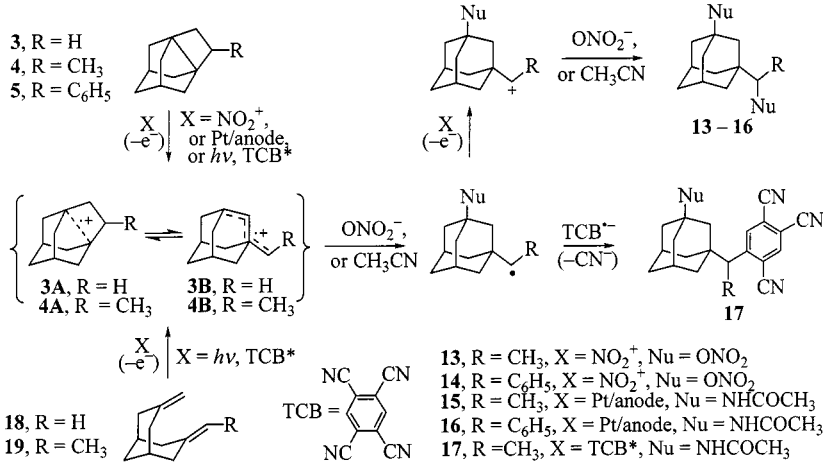
As we have shown previously,[24a,24b] propellanes **1**–**3** may be dinitroxylated with either 100% nitric acid or with $NO_2^+NO_3^-/CH_2Cl_2$ through non-electrophilic mechanisms and hydrocarbon radical cations *do* form in these transformations. Both Equations (4) and (5), modeling this reaction for propellane **3** in the gas phase and in solution by including one solvent molecule (acetonitrile), are exothermic (−51.5 and −37.2 kcal/mol, respectively, at B3LYP). Addition of the second acetonitrile molecule does not change the exothermicity of this reaction significantly. In contrast, the oxidation of hydrocarbon **3** with the NO_3 radical is highly endothermic both in the gas phase [Equation (6)] and in the presence of a solvent molecule [Equation (7)]. Despite of the relative crudeness of this model, it clearly shows the differences in the reactions of propellanes with the nitronium cation and the nitrate radical.

For comparison we generated the radical cations from propellanes **4** and **5** by oxidation with $NO_2^+NO_3^-$ and, independently, by anodic as well as photochemical oxidation. Methyl-substituted propellane **4**, as well as the phenyl-substituted system **5**, only form *rearranged* products under these conditions. The reactions of these two compounds with nitronium reagents occur by SET and lead to rearranged dinitroxy derivatives **13** and **14** (Scheme 2).

Analogous rearrangements were observed under anodic oxidation of **4** and **5** in acetonitrile, where diacetamides **15** and **16** form in a two-step[29] electrochemical/chemical (EC) process. Finally, with such a powerful one-electron oxidant as photoexcited 1,2,3,5-tetracyanobenzene (TCB, oxidation potential 3.44 V[30]), photo-oxidation of propellane **4** in acetonitrile also leads to rearranged product **17**. Hence, we conclude that if radical cation intermediates form in the reactions of **4** and **5**, the homoadamantane cage rearranges rapidly. While the computed barrier for the rearrangement of the non-substituted 3,6-dehydrohomoadamantane radical cation (**3A**) to **3B** is 11.7 kcal/mol at MP2/6-31G*,[31] the transformation of **4A** to **4B** through **TS3** (Figure 2) requires an activation of only 3.6 kcal/mol.

Thus, the reactions of propellanes **4** and **5** with the NO_3 radical, which lead to *unrearranged* dinitroxo derivatives **9** and **10**, are very unlikely to involve hydrocarbon radical cations. It is quite conceivable that propellanes **1**–**3** follow the same mechanisms.

Photo-oxidation of the parent 3,7-dimethylenebicyclo-[3.3.1]nonane (**18**)[31] and 3-ethylidene-7-methylenebicyclo-



Scheme 2. Model single electron transfer oxidations of dehydrohomoadamantanes **3**–**5** and their diolefinic precursors **18** and **19**

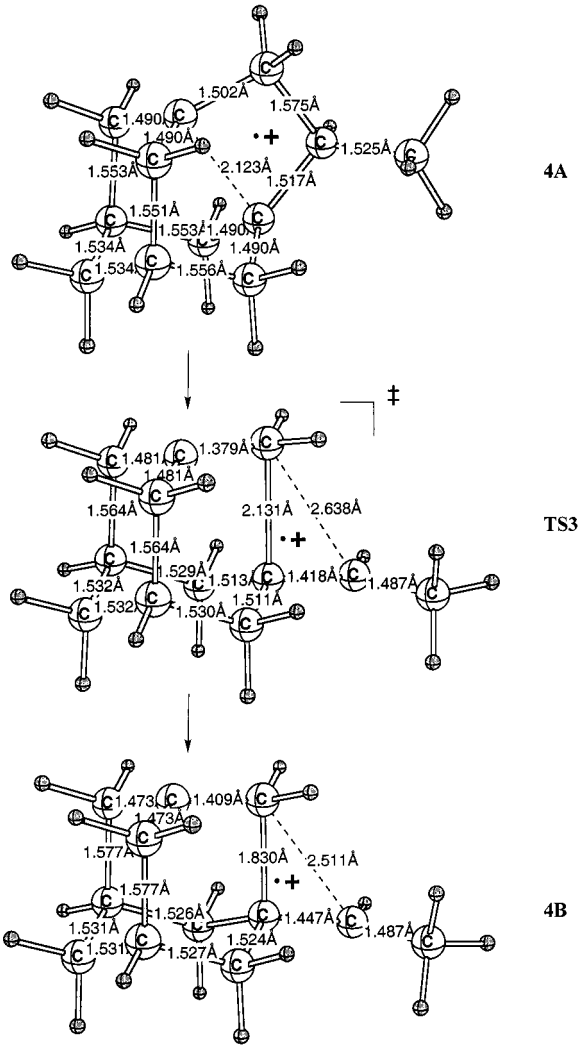


Figure 2. The rearrangement of the 4-methyl-3,6-dehydroadamantane radical cation at MP2/6-31G*

[3.3.1]nonane (**19**) in the presence of TCB gives the same products as found for the photo-oxidations of propellanes **3** and **4**. Thus, oxidation must occur via the same radical cation intermediates (in curly brackets in Scheme 2).

To emphasize this point further, we studied the reactivity of a series of diolefins (**18**−**20**) derived from 3,7-dimethylenebicyclo[3.3.1]nonane with the NO_3 radical produced from CAN under photo-initiation (Scheme 3). In contrast to products formed from photo-oxidation with TCB, acetamino-methyl-nitroxyadamantanes **21**−**23** are derived from a nonoxidative free-radical reaction. Radical addition to diolefin **19** is less regioselective than the addition to the styrene derivative **20**. The analogous formation of adamantane derivatives in the reactions of **18**−**20** with electrophilic radicals was described earlier.[32]

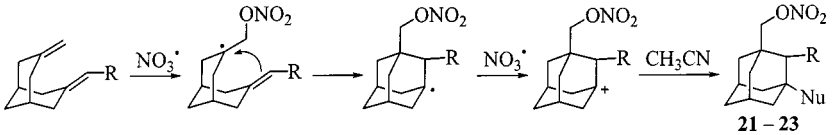
The acetamino derivatives **21**−**23** can only be produced from cage carbocations; these form by further oxidation of the intermediate radicals by CAN, as shown previously for the 1-adamantyl radical.[12]

Conclusions

We examined the reactivity of propellane C−C bonds with NO_3 radicals generated from CAN under mild conditions utilizing photo-initiation in acetonitrile. The structures of the isolated products do not support the formation of propellane radical cations as intermediates. These systems could be generated independently through oxidation with strong SET acceptors or by anodic oxidation and are prone to rearrangement of the substituted homoadamantane cage. As only the *unrearranged* dinitroxy derivatives form in the photoreactions of propellanes **4** and **5** with CAN, there is no evidence for oxidative SET processes in these transformations. This is a consequence of the low oxidation potential of CAN and the NO_3 *radical*, which is simply not hight enough to oxidize saturated hydrocarbons. It therefore seems likely that the C−C activation in cyclopropane and cyclobutane derivatives with CAN under photo-initiation proceeds through S_R2 ring opening: The NO_3 radical may attack the strained hydrocarbon moiety directly.

Experimental Section

General Remarks: Geometries were fully optimized at the B3LYP/6-31G* and MP2/6-31G* levels of theory (unrestricted wavefunctions were used for open-shell species) as implemented in the Gaussian 98[33] program package. Single point energy evaluations with the 6-311+G** basis set were used to improve the energies for the 6-31G* optimized geometries. Harmonic vibrational frequencies were computed to ascertain the nature of all stationary points (the number of the imaginary modes, NIMAG, is 0 for minima and 1 for transition structures). B3LYP/6-31G* energies (Hartrees) and geometries of the transition structures for NO_3 radical addition to phenyl- (**TS1**) and 1,1-dimethylcyclopropane (**TS2**) as well as the MP2/6-31G* energies and geometries for **4A**, **4B**, and **TS3** are collected in the Supporting Information. The energies discussed in the paper refer to the B3LYP/6-311+G**//B3LYP/6-31G* level unless noted otherwise. − NMR spectra were recorded with a Varian VXR-300 spectrometer at 300 MHz (^{1}H NMR), 75 MHz (^{13}C



18, R = H
19, R = CH_3
20, R = Ph

21, R = H, Nu = $NHCOCH_3$
22, R = CH_3, Nu = $NHCOCH_3$
23, R = Ph, Nu = $NHCOCH_3$

Scheme 3. Radical addition reactions of diolefins **18**−**20** with NO_3 radicals

NMR) in $CDCl_3$ solutions. The chemical shifts are given on the δ scale in ppm; internal standard HMDS. − All compounds show appropriate IR and DEPT ^{13}C-NMR spectra. − Melting points are uncorrected.

General Procedure for the Reaction of Hydrocarbons with CAN: 2 mmol of hydrocarbon and 5 mmol of cerium(IV) ammonium nitrate were dissolved in 160 mL of dry acetonitrile and irradiated with a 150-W UV lamp (maximum emission at 300 nm) for 3−10 h until the orange color of the reaction mixture disappeared. The solvent was removed in vacuo at room temperature, the residue was diluted with water (10 mL), extracted with 3 × 20 mL of CH_2Cl_2, and dried with Na_2SO_4. The products were separated by PLC on silica using a mixture of *n*-hexane/ether (1:2) as eluent to give dinitroxy derivatives **6**−**10** and **12**.

1,5-Dinitroxybicyclo[3.3.1]nonane (6): This compound was identical to the material described earlier[34] (yield 360 mg, 73%).

1,5-Dinitroxybicyclo[3.3.2]decane (7): Yield 450 mg, 86%. − ^{1}H NMR: δ = 1.80−1.93 (m, 4 H), 1.95−2.10 (m, 4 H), 2.19 (s, 4 H), 2.25−2.40 (m, 4 H). − ^{13}C NMR: δ = 19.9, 29.4, 35.9, 96.1. − M.p. 121−122 °C (hexane). − $C_{10}H_{16}N_2O_6$ (260.2): calcd. C 46.15, H 6.20, N 10.76; found C 46.01, H 6.35, N 10.57.

3,6-Dinitroxyhomoadamantane (8): This compound was identical to the material described earlier[34] (yield 365 mg, 67%).

4-Methyl-3,6-dinitroxyhomoadamantane (9): Yield 446 mg, 78%. − ^{1}H NMR: δ = 1.05 (d, *J* = 6.4 Hz, 3 H), 1.60−1.75 (m, 4 H), 1.80−2.20 (m, 6 H), 2.30−2.45 (m, 2 H), 2.60−2.75 (m, 2 H), 2.82−3.05 (m, 1 H). − ^{13}C NMR: δ = 17.9, 28.1, 28.2, 32.9, 34.4, 35.5, 37.6, 42.2, 43.2, 43.4, 92.6, 94.4. − M.p. 85−87 °C (hexane). − $C_{12}H_{18}N_2O_6$ (286.3): calcd. C 50.35, H 6.34, N 9.79; found C 50.10, H 6.20, N 9.61.

3,6-Dinitroxy-4-phenylhomoadamantane (10): Yield 495 mg, 71%. − ^{1}H NMR: δ = 1.71−1.79 (m, 2 H), 1.82−1.93 (m, 1 H), 2.00−2.21 (m, 3 H), 2.27−2.61 (m, 6 H), 2.77−2.89 (m, 1 H), 2.90−2.99 (m, 1 H), 3.95−4.05 (m, 1 H), 7.22−7.32 (m, 5 H). − ^{13}C NMR: δ = 28.3, 28.4, 34.6, 35.4, 37.0, 43.7, 43.9, 44.56, 48.7, 92.2, 92.6, 127.4, 128.5, 128.6, 140.2. − M.p. 127−128 °C (hexane). − $C_{17}H_{20}N_2O_6$ (348.4): calcd. C 58.61, H 5.79, N 8.04; found C 58.74, H 5.80, N 7.82.

2,4-Dinitroxyadamantane (12): Mixture of diastereomers (*exo*,*exo*/*exo*,*endo* = 1:4), yield 460 mg, 89%. − ^{1}H NMR: δ = 1.58−1.80 (m, 2 H), 2.80−2.37 (m, 8 H), 2.52−2.60 (m, 2 H), 5.05−5.12 (m, 0.25 H), 5.18−5.30 (m, 1.75 H). − ^{13}C NMR of ***exo*,*exo*-12**: δ = 25.4, 26.0, 29.6, 30.8, 32.3, 33.7, 82.3. − ^{13}C NMR of ***exo*,*endo*-12**: δ = 25.3, 29.8, 29.9, 30.5, 30.6, 30.8, 33.9, 35.5, 81.1, 86.2. − $C_{10}H_{14}N_2O_6$ (258.2): calcd. C 46.51, H 5.46, N 10.85; found C 46.29, H 5.71, N 10.92.

Oxidation of Propellanes 4 and 5 with $NO_2^+NO_3^-$ in 100% HNO_3 and CH_2Cl_2: A solution of 500 mg of the hydrocarbon in 2.5 mL of CH_2Cl_2 was added dropwise to a mixture of 5 mL of 100% HNO_3 and 2.5 mL of CH_2Cl_2 at −10 °C. The mixture was kept at −10 °C for 10 min and then poured onto ice. The mixture was extracted with CH_2Cl_2 (3 × 5 mL), the combined extracts were washed with water, $NaHCO_3$ solution, brine, dried with Na_2SO_4 and the solvent was removed in vacuo. Products were separated by PLC on silica using a mixture of *n*-hexane/ether (1:3.5) as eluent to give dinitroxy derivatives **13** and **14**.

1-Nitroxy-3-(1-nitroxyethyl)adamantane (13): This compound was identical to the material described earlier[24b] (yield 644 mg, 73%).

1-Nitroxy-3-(1-nitroxybenzyl)adamantane (14): Yield 427 mg, 55%. − ^{1}H NMR: δ = 1.50−1.63 (m, 4 H), 1.65−1.82 (m, 2 H), 1.90−2.20 (m, 6 H), 2.31−2.40 (m, 2 H), 5.43 (s, 1 H), 7.21−7.40 (m, 5 H). − ^{13}C NMR: δ = 30.2, 34.8, 36.8, 36.8, 38.8, 40.3, 40.7, 89.5, 90.9, 127.4, 128.3, 128.9, 134.0. − $C_{17}H_{20}N_2O_6$ (348.4): calcd. C 58.61, H 5.79, N 8.04; found C 58.47, H 5.99, N 7.90.

General Procedure for the Electro-Oxidation of Hydrocarbons 4 and 5: A mixture of 1 mmol of hydrocarbon, 75 mL of acetonitrile, and 200 mg of NH_4BF_4 was placed into a glass cell with platinum electrodes and subjected to direct current at 2.5 V anode potential for 6 h. The reaction mixture was diluted with 10 mL of water and the acetonitrile solvent was evaporated in vacuo. The mixture was extracted with CH_2Cl_2, the combined extracts were washed with water, brine, dried with Na_2SO_4 and the solvent was evaporated. The residue was purified by PLC on silica using a mixture of ether/methanol (10:1) as eluent, which gave diacetamides **15** (from **4**) and **16** (from **5**).

1-Acetamino-3-(1-acetaminoethyl)adamantane (15): Yield 220 mg, 79%. − ^{1}H NMR: δ = 1.05 (d, *J* = 6.6 Hz, 3 H), 1.40−1.65 (m, 6 H), 1.72−1.82 (m, 2 H), 1.93 (s, 3 H), 2.03 (s, 3 H), 1.85−2.00 (m, 4 H), 2.18 (br. s, 2 H), 3.80 (m, 1 H), 5.46 (br. s, 1 H), 5.66 (br. s, 1 H). − ^{13}C NMR: δ = 14.7, 23.5, 24.5, 29.1, 35.6, 37.2, 37.6, 38.0, 40.8, 41.1, 41.7, 52.3, 52.5, 169.6, 169.7. − $C_{16}H_{26}N_2O_2$ (278.4): calcd. C 69.03, H 9.41, N 10.06; found C 69.27, H 9.43, N 10.27.

1-Acetamino-3-(1-acetaminobenzyl)adamantane (16): Yield 221 mg, 65%. − ^{1}H NMR: δ = 1.20−1.65 (m, 6 H), 1.67−2.15 (m, 8 H), 1.86 (s, 3 H), 1.97 (s, 3 H), 4.7 (d, *J* = 9.3 Hz, 1 H), 5.70 (br. s, 1 H), 5.80 (d, *J* = 9.3 Hz, 1 H), 7.03−7.30 (m, 5 H). − ^{13}C NMR: δ = 23.3, 24.5, 29.0, 29.10, 35.5, 37.4, 38.2, 38.5, 40.6, 40.7, 42.3, 52.4, 61.8, 127.0, 127.7, 128.4, 131.9, 138.8, 169.7, 169.9. − M.p. 172−173 °C (hexane). − $C_{21}H_{28}N_2O_2$ (340.5): calcd. C 74.08, H 8.29, N 8.23; found C 73.85, H 8.51, N 8.00.

Photo-Oxidation of 4 and 19 with TCB: A solution of 162 mg (1 mmol) of the hydrocarbon and 150 mg (0.84 mmol) of TCB in 120 mL of acetonitrile was irradiated under argon with a 150-W lamp (maximum emission at 300 nm) for 5 h. The reaction mixture was diluted with 5 mL of water and the solvents were removed in vacuo. Chromatographic separation on silica with ethyl acetate/cyclohexane gave unchanged TCB (96 and 80 mg, respectively from the oxidation of **4** and **19**). Elution with ethyl acetate/methanol (20:1) gave 74 mg (20% from **4**) and 95 mg (25% from **19**) of 1-(3-acetaminoadamant-1-yl)-1-(2,4,5-tricyanophenyl)ethane (**17**). − ^{1}H NMR: δ = 1.31 (d, *J* = 7.5 Hz, 3 H), 1.30−1.43 (m, 2 H), 1.45−1.90 (m, 8 H), 1.93−2.05 (m, 2 H), 2.15−2.33 (m, 2 H), 2.30 (s, 3 H), 3.18 (q, *J* = 7.5 Hz, 1 H), 5.70 (br. s, 1 H), 7.73 (s, 1 H), 8.03 (s, 1 H). − ^{13}C NMR: δ = 14.3, 20.3, 20.6, 30.0, 30.2, 30.7, 41.7, 42.5, 44.8, 47.8, 50.6, 113.6, 114.3, 114.4, 115.3, 118.7, 118.9, 133.9, 136.8, 154.0. − $C_{23}H_{24}N_4O$ (372.5): calcd. C 74.17, H 6.49, N 15.04; found C 74.47, H 6.13, N 15.47.

Reaction of Dienes 18−20 with CAN: The reactions were carried out using the same procedures as described above for the reactions of the propellanes with CAN.

1-Acetamino-3-nitroxymethyladamantane (21): Yield 311 mg, 58%. − ^{1}H NMR: δ = 1.45−1.63 (m, 4 H), 1.50−1.70 (m, 2 H), 1.81−2.05 (4 H), 1.84 (s, 2 H), 1.87 (s, 3 H), 2.10−2.25 (br. s, 2 H), 4.15 (s, 2 H), 5.61 (br. s, 1 H). − ^{13}C NMR: δ = 24.5, 28.8, 35.3, 35.4, 37.9, 40.8, 42.4, 51.8, 81.2, 169.5. − M.p. 97−100 °C (hexane). $C_{13}H_{20}N_2O_4$ (268.3): calcd. C 58.19, H 7.51, N 10.44; found C 57.89, H 7.54, N 10.65.

1-Acetamino-2-methyl-3-nitroxymethyladamantane (22): This compound was formed together with its isomer 1-acetamino-3-(1-nitroxyethyl)adamantane (ratio 1:2), yield 378 mg, 67%. – ^{1}H NMR: δ = 0.91 (d, *J* = 7 Hz, 1 H), 1.42 (d, *J* = 7 Hz, 2 H), 1.35–1.64 (m, 6 H) 1.65–2.00 (m, 5 H), 1.84 (s, 2 H), 1.88 (s, 1 H), 2.05–2.19 (m, 2 H), 4.18 (q, *J* = 9 Hz, 1 H), 4.27 (q, *J* = 7 Hz, 1 H), 5.57 (br. s, 1 H). – ^{13}C NMR: δ = 9.1, 13.0, 24.2, 24.4, 28.6, 28.7, 30.5, 28.9, 35.4, 35.5, 36.3, 36.7, 36.8, 37.2, 37.8, 38.3, 40.5, 40.6, 40.9, 41.4, 41.6, 52.0, 52.2, 84.9, 92.1, 169.3, 169.6.

1-Acetamino-3-nitroxymethyl-2-phenyladamantane (23): Yield 392 mg, 57%. – ^{1}H NMR: δ = 1.47 (s, 3 H), 1.60–1.83 (m, 6 H), 1.83–2.00 (m, 2 H), 2.11–2.43 (m, 4 H), 2.87–2.93 (m, 1 H), 3.89 (dd, J_1 = 14 Hz, J_2 = 3 Hz, 2 H), 4.83 (s, 1 H), 7.23–7.40 (m, 5 H). – ^{13}C NMR: δ = 24.1, 28.7, 29.1, 33.9, 36.2, 36.4, 39.2, 41.1, 42.2, 55.6, 56.0, 85.5, 127.1, 127.5, 128.3, 128.7, 133.6, 138.1, 169.7. – M.p. 146–147 °C (hexane). – $C_{19}H_{24}N_2O_4$ (344.4): calcd. C 66.26, H 7.02, N 8.13; found C 66.29, H 7.32, N 8.02.

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