

The quantum-chemical modeling of adamantane olefination with ethylene, propylene, butylene

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Introduction

Adamantane is a hydrocarbon with formula $C_{10}H_{16}$ (or tricyclo[3.3.1.1^{3,7}]decane, according to a systematic nomenclature). Adamantane and its derivatives possess cage-like skeletons with T_d point group of molecule is. The empirical formula describing these class of hydrocarbons is $C_{4n+6}H_{4n+12}$, where n means a number of cage carbon atoms. Such type of structures turns out to be rigid. However, this system is strain-free¹.

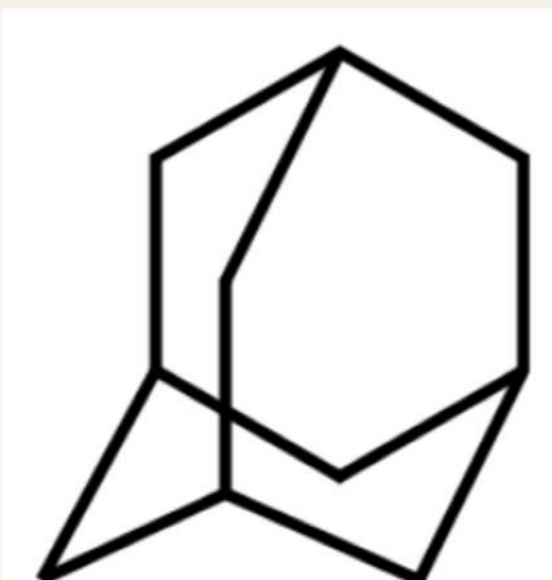
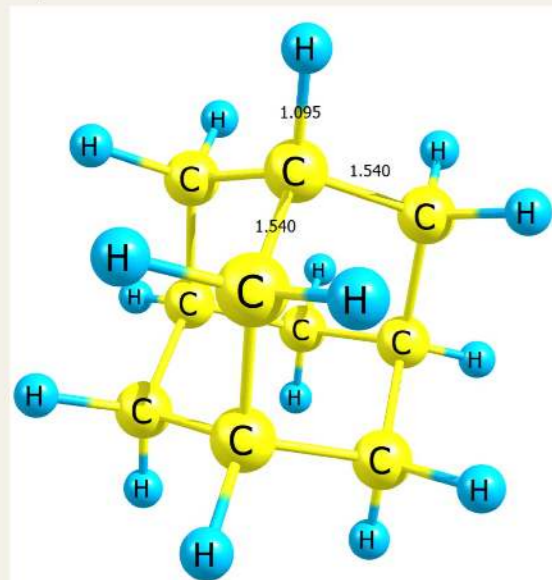


Figure 1. 3D and 2D model of adamantane molecule (AdH). Bond lengths are giving in Angstroms.

Unsaturated adamantanes

Among the most important and promising lines of research in adamantane chemistry are those involving double-bonded adamantane derivatives. The high reactivity of these compounds is one of the strongest arguments in favour of utilizing them as starting materials for the synthesis of various functional adamantane derivatives, monomers, thermally stable and high-energy fuels and oils, bioactive compounds, pharmaceuticals, and higher diamond-like bulky polymers such as diamondoids. Our recent review considers obtaining and the usage of adamantane unsaturated compounds¹.

The increasing interest in the synthesis and downstream processing of unsaturated adamantane derivatives has been motivated by the high potential of these compounds as monomers for polymerization and as starting materials for pharmaceuticals, bioactive agents, optical materials, and other products. On the other hand, there is a lack of information concerning the production of alkenyladamantanes directly from adamantane, which can probably be explained by the challenges in the search for appropriate reaction conditions and catalysts to produce high yield unsaturated derivatives. Unfortunately, it has not been reported on the synthesis of higher diamondoids from unsaturated adamantane derivatives. These compounds have been produced solely from some grades of crude oils and gas condensates. A relevant studies relying on quantum-chemical calculations is needed to gain insight into the reaction mechanisms and the patterns of the synthesis of unsaturated adamantane derivatives.

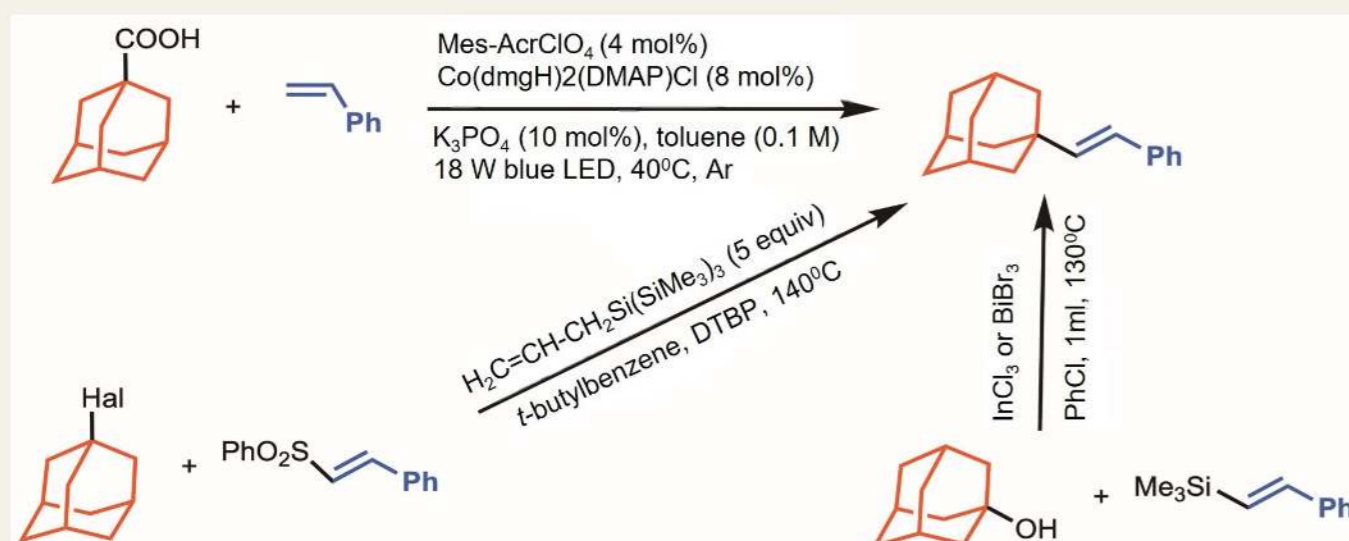


Figure 2. Examples of reactions for for obtaining unsaturated adamantane derivatives.¹

Adamantane alkenylation with olefins

The object of this study is a chemical interaction of adamantane with simple unsaturated hydrocarbons, such as ethylene C_2H_4 , propylene C_3H_6 , and 1-butylene C_4H_8 . Commonly, the addition of alkenes to hydrocarbons leads to the production of alkanes. Nevertheless, in case of ionic alkylation of adamantane, unsaturated products also occur. The yield of such substances depends on the reaction conditions and a catalysator composition². We used aluminum chloride as an example of catalysator in our quantum-chemical calculations. The first stage in all reactions is the loss of hydrogen anion which let us obtain tertiary 1-adamantyl cation.

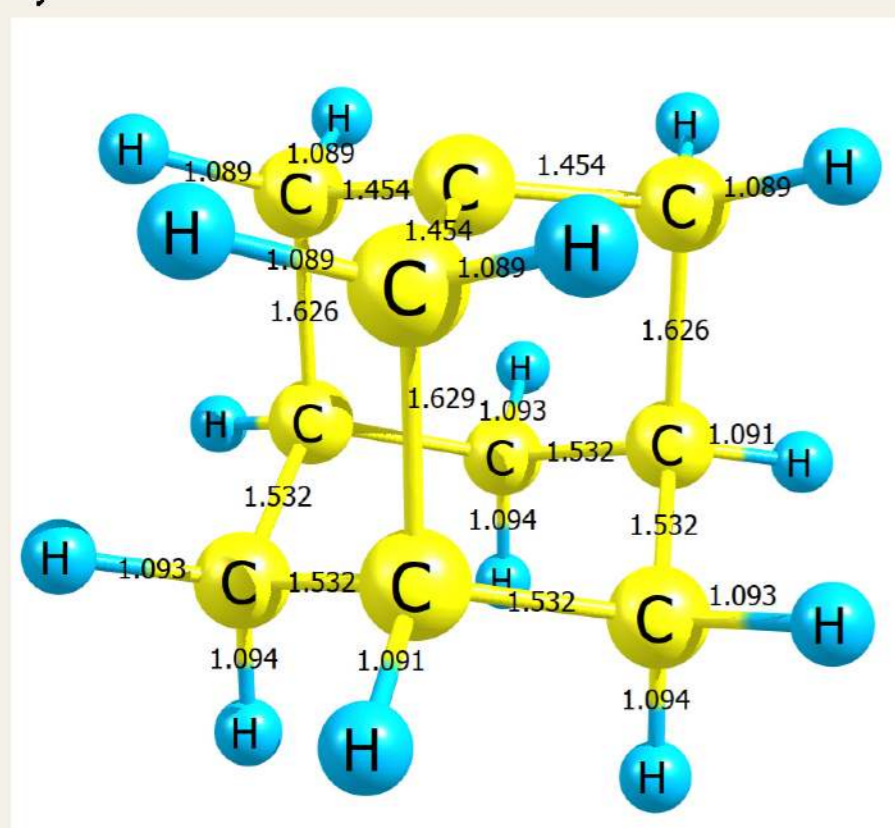


Figure 3. 1-Adamantyl cation. Bond lengths are giving in Angstroms.

Computational methods

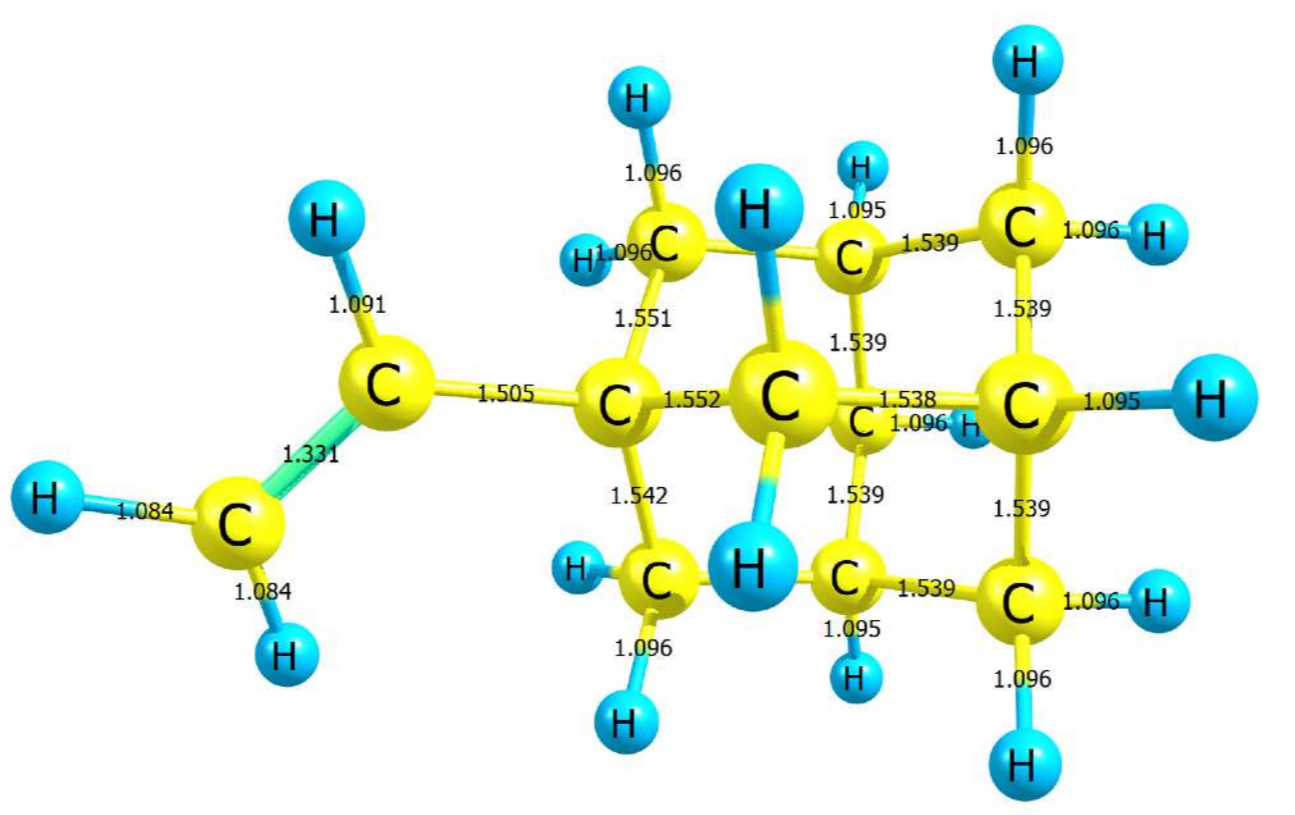
The geometry optimization and normal-mode analysis for the studied systems were carried out using B3LYP-D3(BJ) functional with 6-311++G* basis set as implemented in Gamess US program. Grimme's dispersion correction was used for accounting long-range correlation. The theoretical calculations of harmonic frequencies were conducted to determine the minima (no imaginary frequencies) and saddle points (1 imaginary frequency). All thermal corrections are calculated at 298 K. The intrinsic reaction coordinate (IRC) method was used to confirm the correspondence of the transition state to a certain reaction. The visualization of the results of the calculations is performed using Chemcraft computer program.

Structure of products

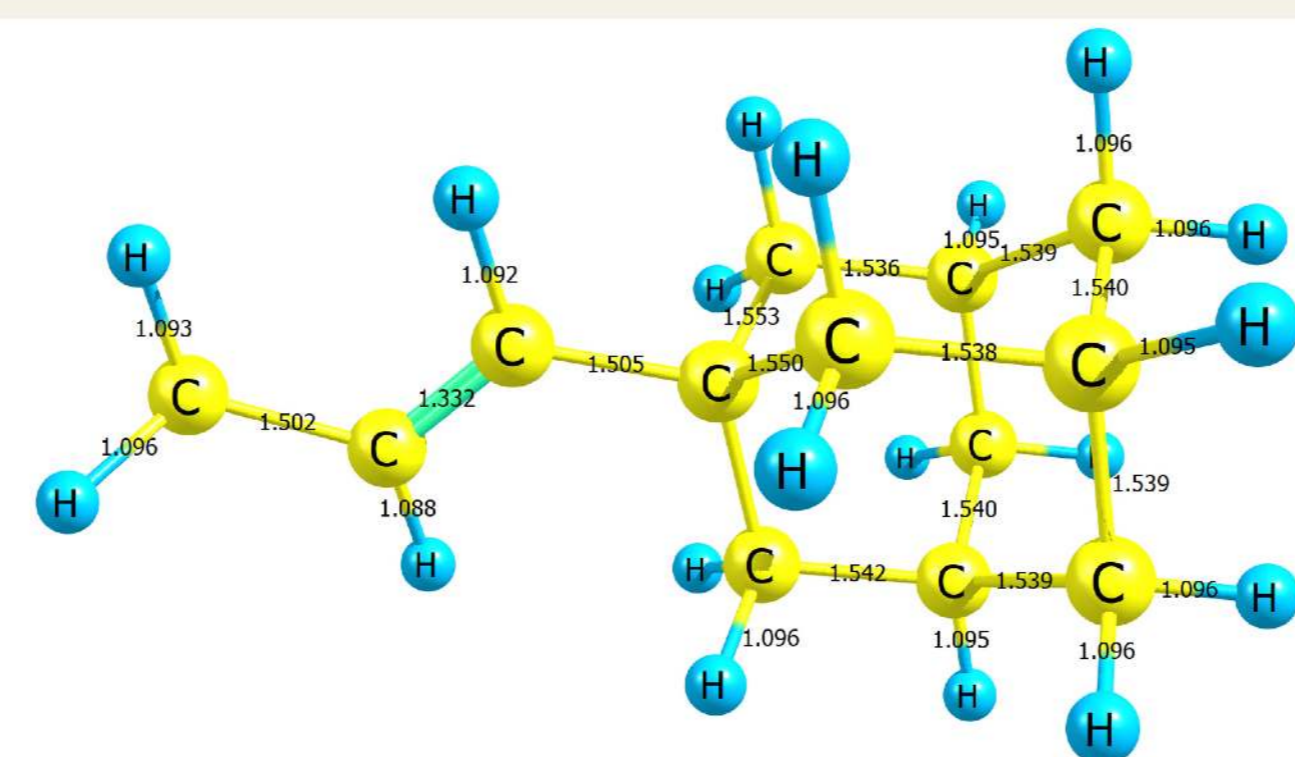
Changes in Gibbs free energy upon chemical transformations can be seen from the table 1.

Reaction	ΔG , kcal/mol (298.15 K)
$AdH + C_2H_4 = Ad-CH=CH_2 + H_2$	7.92
$AdH + C_3H_6 = Ad-CH=CH-CH_3 (trans) + H_2$	9.42
$AdH + 1-C_4H_8 = Ad-CH=CH-CH_2-CH_3 (trans) + H_2$	10.64
$Ad + 1-C_4H_8 = Ad-CH_2-CH=CH-CH_3 (trans) + H_2$	8.19
$Ad + 1-C_4H_8 = Ad-CH_2-CH_2-CH=CH_2 (trans) + H_2$	12.27
$Ad + 1-C_4H_8 = Ad-CH=CH-CH=CH_2 + 2H_2$	24.91

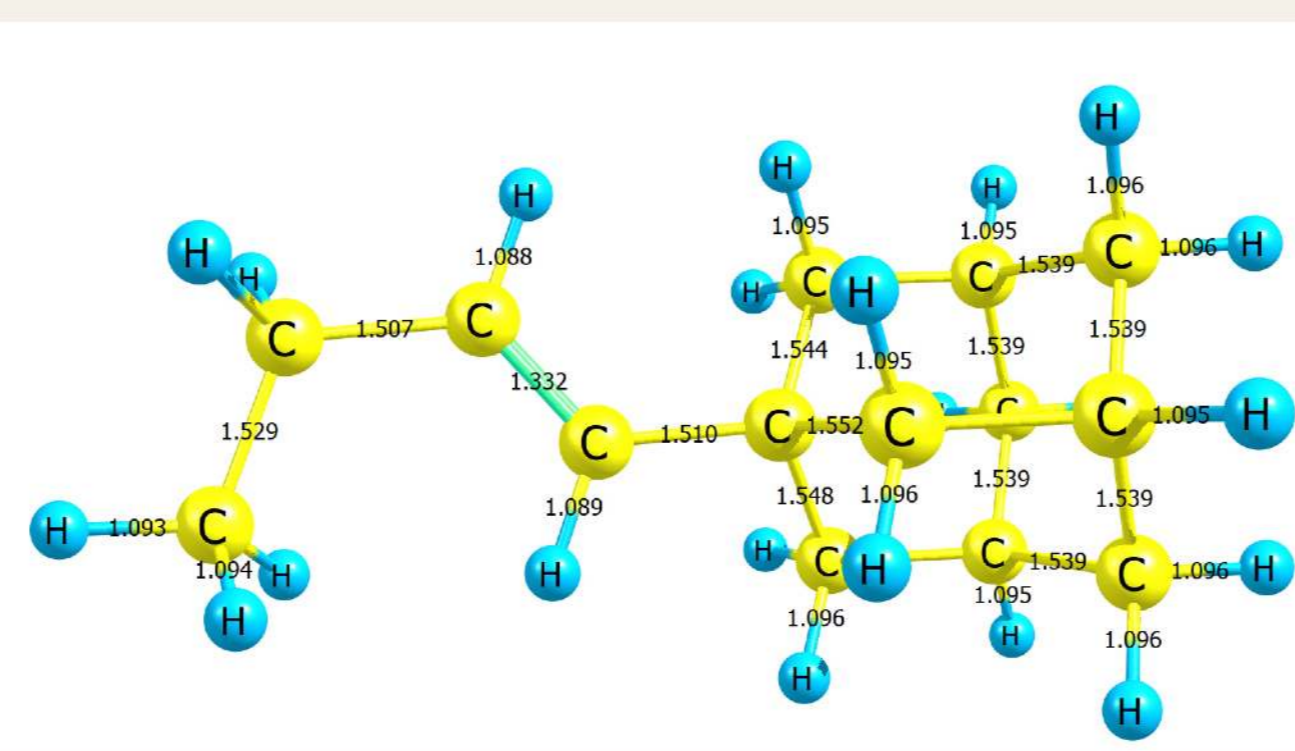
Table 1. Gibbs free energies of reactions. AdH- adamantane ($C_{10}H_{16}$). Ad- $C_{10}H_{15}$.



a



b



c

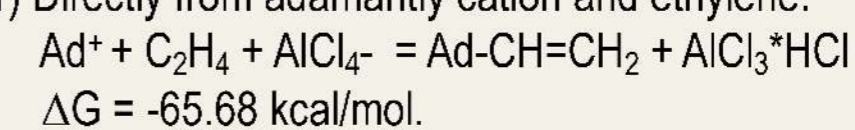
Figure 4. Some products of adamantane alkenylation: a) vinyladamantane, b) 1-n-propenyladamantane, c) 1-n-butyleneadamantane. Bond lengths are giving in Angstroms.

An increase in the acid strength of the catalyst and a decrease in the process temperature will promote the yield of the unsaturated product in the catalytic alkylation reaction of adamantane. According to experimental data, the yield of unsaturated adamantanes drops with an increase in the molecular weight of the olefins.

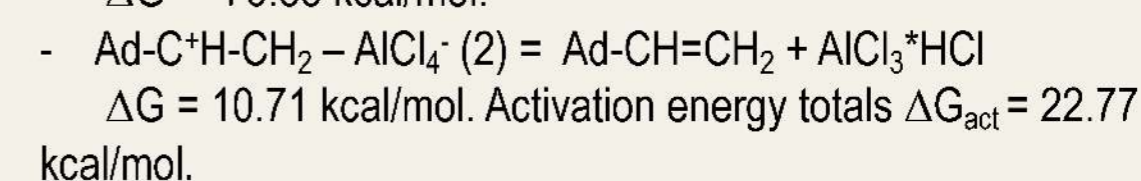
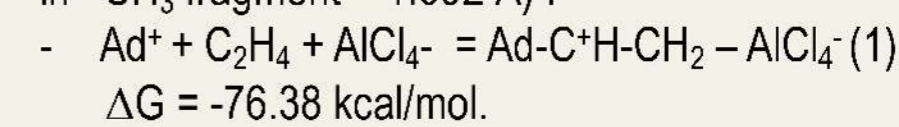
Alkene formation

Ethyleneadamantane (vinyladamantane) may occur in several ways.

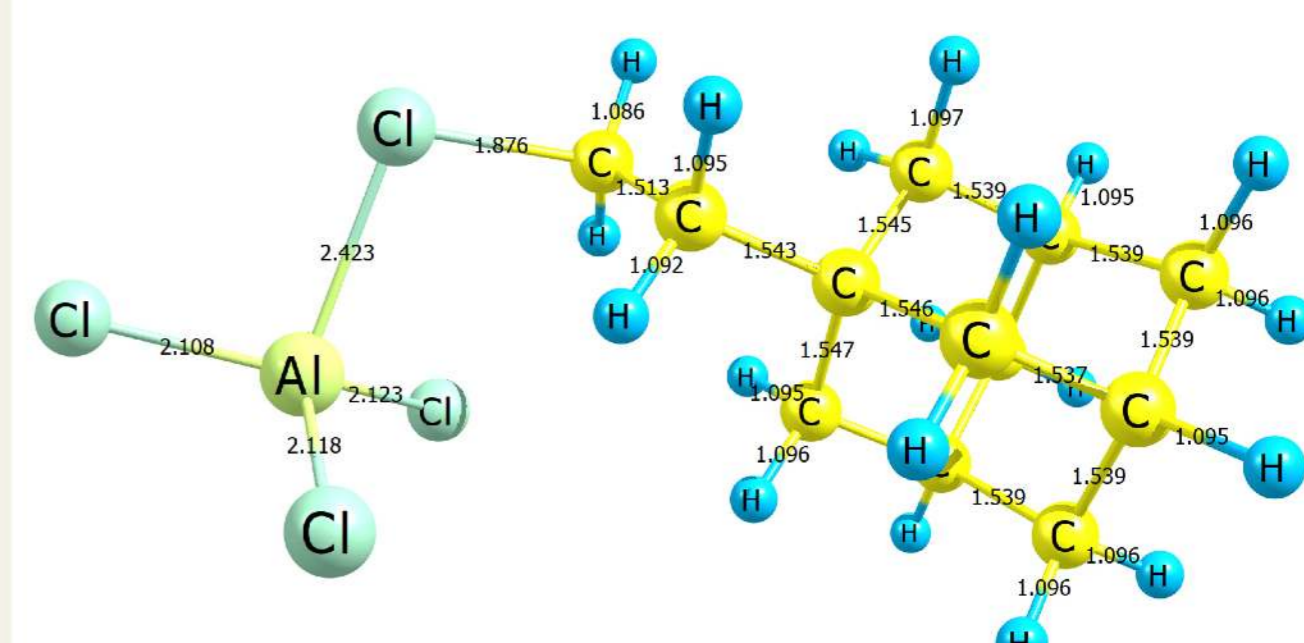
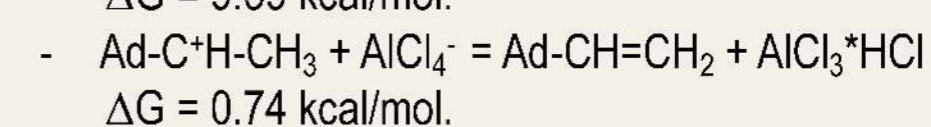
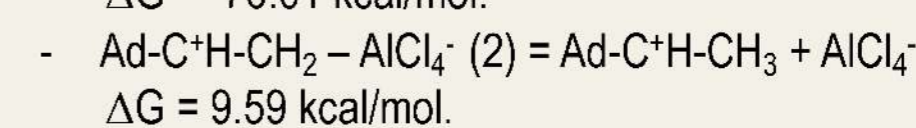
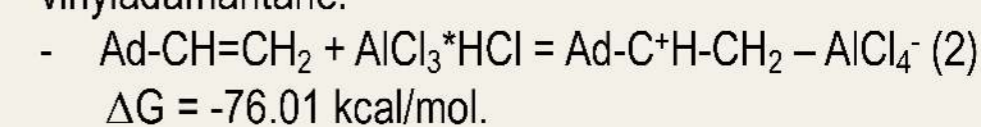
1) Directly from adamantyl cation and ethylene:



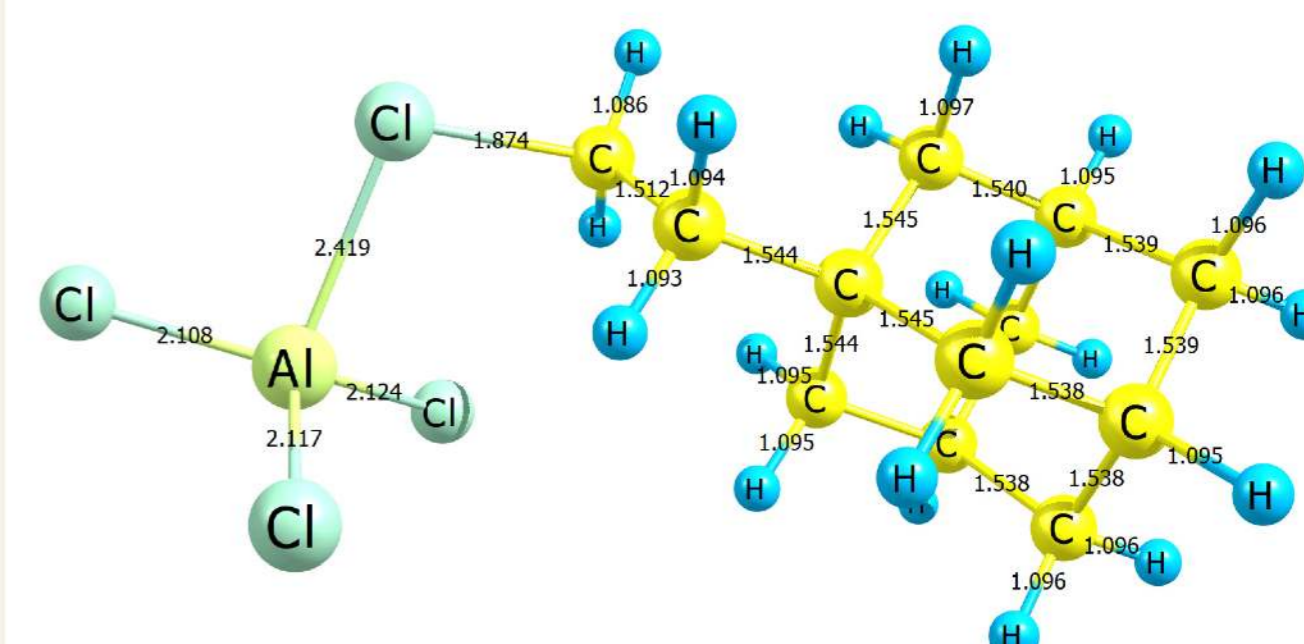
2) In one stage from $Ad-C^+H-CH_2 - AlCl_4^-$ (1, structure with C-H distance in $-CH_3$ fragment – 1.092 Å) :



3) Obtained earlier vinyladamantane might transform in $Ad-C^+H-CH_2 - AlCl_4^-$ (2, structure with enlarged C-H distance in $-CH_3$ fragment – 1.135 Å). Such cation also decomposes into vinyladamantane:



(1)



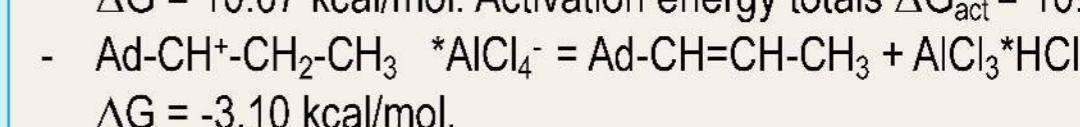
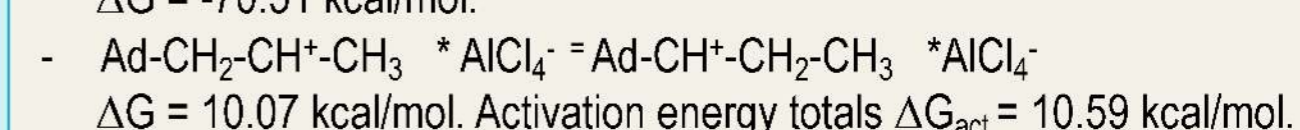
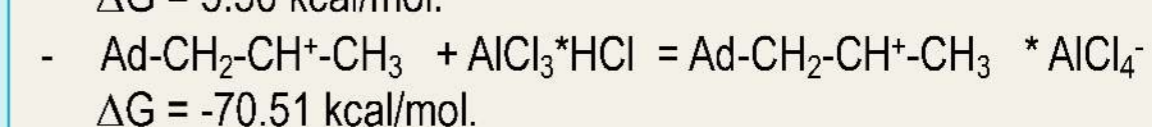
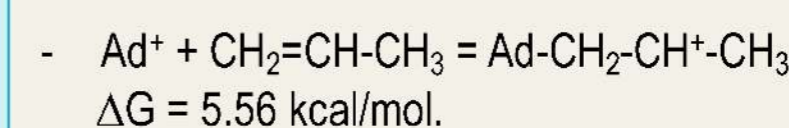
(2)

Figure 5. Structure of cations:

- (1) $Ad-C^+H-CH_2 - AlCl_4^-$
- (2) $Ad-C^+H-CH_2 - AlCl_4^-$

The peculiarity of adamantane interaction with ethylene is the fact that there is no minima corresponding to $Ad-CH_2-CH_2^+$ cation. Similar structures are obtained with adamantane olefination with alkenes with greater molar mass.

Earlier it was found out that the scheme of 1-n-propenyladamantane formation from 1-adamantyl cation is as follows³:



Literature

¹ Baranov. N.I., Bagrii. E.I., Safir, R.E. et al., Pet. Chem., 2022, 62, 352-375. <https://doi.org/10.1134/S0965544122020153>.

² Bagrii, E. I. *Adamantany: poluchenie, svoystva, primeneniye* (Adamantanes: synthesis, properties, applications), Moscow: Nauka, 1989. chemspider.com/Chemical-Structure.8883.html

³ Baranov. N.I., Safir, R.E., Bagrii. E.I., et al., Pet. Chem., 2020, 60, 1033-1042. <https://doi.org/10.1134/S0965544120090042>.