Short Communication

Derivatisation of Saturated Hydrocarbons: A Facile One-step Formation of N-(1-Adamantyl)acetamide from Adamantane

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In several substitution reactions at the 1-position of adamantane, the 1-adamantyl cation appears to be an intermediate. For example, the halogenation of adamantane is catalysed by Lewis acids but not by radical-chain initiators.[1,2] In other reactions, the tert-butyl cation (from tert-butyl alcohol or tert-butyl chloride) has been used for the formation of the 1-adamantyl cation which in turn reacts with nucleophiles in the product-forming step.[3–5]

The formation of the 1-adamantyl cation is, in effect, an oxidation of the 1-carbon atom of adamantane. Nitric acid is a convenient oxidant for several hydrocarbons[6] and adamantane has been reported to give 1-adamantyl nitrate with this reagent.[7,8] However, organic nitrates are unstable compounds, not well suited as intermediates for chemical syntheses, especially not on a larger scale.[9]

Nitriles react with carbocations in Ritter reactions to give the corresponding N-substituted amides. They are reported to react with the 1-adamantyl cation to form N-(1-adamantyl)amides.[4,10–12] Adamantane itself has been reported to react with a mixture of nitric acid, acetonitrile and hydrobromic acid (presumably for the formation of 1-adamantyl bromide) to give N-(1-adamantyl)acetamide.[12] However, if nitric acid generates the 1-adamantyl carbocation from adamantane, the presence of hydrobromic acid (or any other auxiliary nucleophile) would not be necessary for the formation of the amide. We have, accordingly, treated adamantane with nitric acid and acetonitrile without any auxiliary nucleophiles present. For comparison, we also treated endo-tetrahydrodicyclopentadiene under the same conditions. This compound reacted in a manner similar to adamantane with ruthenium tetraoxide to give endo-tetrahydrodicyclopentadien-2-ol.[13]

The results are given in Table 1 and clearly show the method to give good yields for the amidation of the 1-position of adamantane. Ruthenium tetraoxide was not necessary for a successful result (run 2). The nitric acid need not be 90 % (see run 3) but the reaction is considerably slower with a 65 % aqueous solution. Furthermore, the presence of an inert solvent, immiscible with the aque-

ous phase, is necessary for an acceptable yield (compare runs 1 and 4). For the analogous reaction with endo-tetrahydrodicyclopentadiene (5), only a moderate yield of the 2-acetamide (13 %) was obtained, presumably because of formation of olefins which undergo further oxidations.

We have reported the derivatisation of adamantane and endo-tetrahydrodicyclopentadiene by RuO_4 oxidations.[13] The yield of adamantan-1-ol was 82 %, that of endo-tetrahydrocyclopentadien-2-ol was 71 %. Considering the cost of the reagents (RuO_4–$NaIO_4$ vs. HNO_3), the amidation reaction of adamantane presented here must be regarded as advantageous for the derivatisation of adamantane.

Experimental

The reactions were run with magnetic stirring. Introductory runs with 90 % nitric acid indicated the reactions of adamantane to be complete after 4–5 h. The reactions were quenched by the addition of water, the products were extracted with dichloromethane, and the resulting solution was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4 before the solvents were evaporated off. The yields in

Table 1. Results from the reactions of hydrocarbons (RH) with nitric acid and acetonitrile at 25 °C for 5 h.

Run	R	Yields of RNHCOCH$_3$
1[a]	1-Adamantyl	74
2[b]	1-Adamantyl	69
3[c]	1-Adamantyl	9
4[d]	1-Adamantyl	19
5[e]	2-endo-Tetrahydrodicyclopentadienyl	13

[a]Adamantane (80 mg), acetonitrile (1 ml), tetrachloromethane (3 ml), nitric acid (90 %, 3 ml). [b]As for [a] but with $RuO_2 \cdot xH_2O$ (5 mg). [c]As for [a] but with 65 % nitric acid; 80 % adamantane recovered. [d]As for [a] but without tetrachloromethane. [e]Reaction conditions as for [a]. Product: N-(2-tetrahydrodicyclopentadienyl)-acetamide.

Table 1 are from GC analyses (25 m fused silica/SE-30, p-nitrotoluene as an internal standard). The products were identified by comparing the melting points and spectral properties with those of authentic samples.[1]

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