Pyrolysis of 3-Homoadamantyl Acetate to 4-Methyleneprotoadamantane and 3-Vinylnoradamantane

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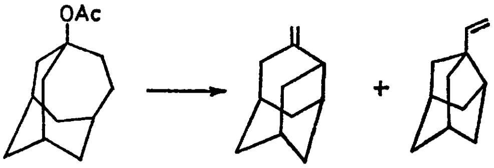
Summary Pyrolysis of 3-homoadamantyl acetate at 500—600 °C yielded 4-methyleneprotoadamantane and 3-vinylnoradamantane, which were converted into various derivatives by ozonolysis, hydrogenation, and rearrangement.

Ester pyrolysis in the gas phase is generally used to introduce a double bond without isomerization. Rearrangement is an uncommon occurrence during thermal elimination reactions as evidenced by the few known cases, most of which involve a ring system.[1] We wish to report the formation of two rearranged products from the pyrolysis of 3-homoadamantyl acetate (**1**).[2,3] No previous ester thermolysis has been disclosed for the homoadamantyl structure. The conditions entailed passage of the vapour (*ca.* 2 g) during 2—4 h through a 19 × 750 mm Vycor tube containing Vycor chips at 500—600 °C with nitrogen as the carrier gas.

Reaction afforded 4-methyleneprotoadamantane (**2**), b.p. 209 °C, and 3-vinylnoradamantane (**3**), b.p. 190 °C, in combined yields of 30—40%, which were separated by preparative g.l.c. The ratio of (**1**) : (**2**) varied in the range of 2—3 : 1. This provides a novel method of forming the proto- and nor-adamantane structures, in addition to affording versatile precursors for conversion into various derivatives.

Compounds (**2**) and (**3**) were transformed by ozonolysis into 4-protoadamantanone[4] and 3-noradamantanecarboxaldehyde, m.p. 130—133 °C. LiAlH$_4$ reduction of the carbonyl-containing mixture provided three isomeric alcohols, 4-hydroxyprotoadamantane (*exo–endo*)[5] and 3-noradamantylmethanol.[6] Compound (**2**) was synthesised from 4-protoadamantanone by the Wittig method (10%).

Hydrogenation of the olefin mixture over Pd on charcoal produced 4-methylprotoadamantane (*endo*, b.p. 209 °C-*exo*) and 3-ethylnoradamantane, b.p. 195 °C. The major isomer of the product from (**2**) was assigned the *endo* configuration by analogy to hydride reduction of 4-protoadamantanone.[5]



(**1**) (**2**) (**3**)

Rearrangement of pure (**2**) with formic acid in ether at reflux gave 1-methyl-2-adamantyl formate, b.p. 253°. The mechanistic aspects are presumably analogous to those for acid-catalysed rearrangement of 4-methylprotoadamantan-4-ol to 1-methyladamantan-2-ol.[5] Hydrolysis afforded the corresponding alcohol.[5] Under identical rearrangement conditions (**3**) remained unchanged.

New compounds were characterized by microanalyses and spectral data.

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