

**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.

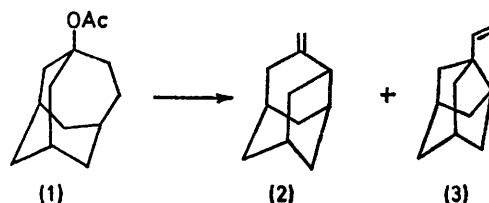
ESTER pyrolysis in the gas phase is generally used to introduce a double bond without isomerization. Rearrangement is an uncommon occurrence during thermal elimination reactions as evidenced by the few known cases, most of which involve a ring system.¹ We wish to report the formation of two rearranged 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-protoadamantanone⁴ and 3-noradamantanecarboxaldehyde, m.p. 130–133 °C. LiAlH₄ 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



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.

We thank the National Science Foundation and the Graduate School, University of Wisconsin-Milwaukee, for financial support, and Dr. P. v. R. Schleyer and Dr. D. Lenoir for a sample of 1-methyladamantan-2-ol.

(Received, 18th October 1972; Com. 1780.)

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