

PYROLYSIS OF HOMOADAMANT-3-ENE¹

Theodorus C. Klebach and Maitland Jones, Jr.*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

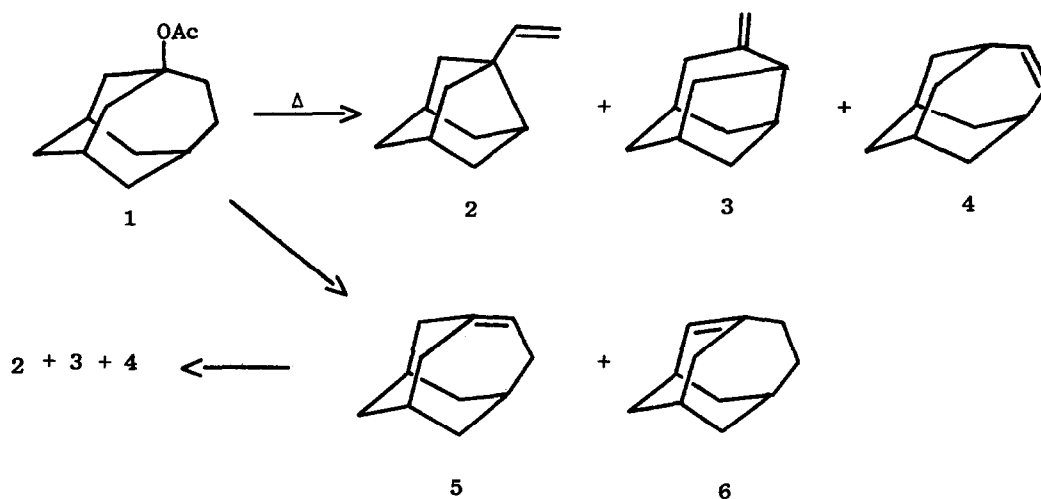
Peter Kovacic

Department of Chemistry, University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

SUMMARY: Pyrolysis of homoadamant-3-ene (5), generated from 1-adamantylcarbene (7), leads to the same three olefins (2, 3, and 4) that are produced from pyrolysis of 3-homoadamantyl acetate (1).

Although it is agreed that pyrolysis of 3-homoadamantyl acetate (1) produces three rearranged hydrocarbons, 2, 3, and 4,²⁻⁴ no such agreement attends the mechanistic interpretation of these results. Several rearrangements involving both six- and seven-membered transition states have been suggested by Kwart and Slutsky.² The seven-membered formulation has been subsequently criticized by Taylor, who proposed a combination of processes entailing carbon-carbon bond migrations and acetate rearrangements, all of which were characterized by the more normal six-membered transition states.³

Earlier it had been proposed by Adams and Kovacic that acetate pyrolysis led initially in a classical fashion to bridgehead alkenes 5 and 6.⁴ Secondary rearrangement was thought to proceed through breaking of allylic bonds and subsequent recombination of diradicals.⁴ The results of deuterium labeling studies⁴ have been used to support the various views of the reaction.



We have been able to isolate 5, one of the two compounds containing a bridgehead double bond postulated by Adams and Kovacic,⁴ from ring expansion of 1-adamantylcarbene 7.⁵ The carbene was produced in conventional fashion by pyrolysis of 1-adamantyl diazomethane.⁵ Generation of 7 at 400°C leads essentially to pure 5 which dimerizes^{6,7} on warming to room temperature. Higher pyrolysis temperatures (ca. 500–520°C) result in formation of the same compounds, 2, 3, and 4, as found in the acetate pyrolyses. The table below gives the percentages of the compounds formed in this and prior work. The compositions were determined by the usual gas chromatographic techniques. Structures followed from comparisons of spectra with those of authentic samples.^{2,4}

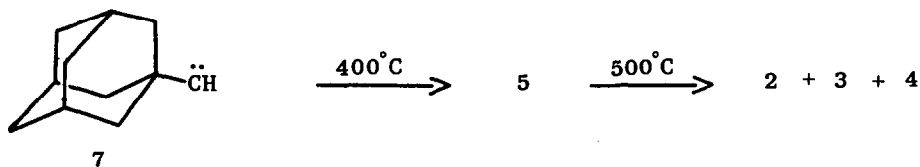


TABLE. PYROLYSIS OF 1 AND 7 LEADING TO 2, 3 AND 4

Experi- ment	Starting Material	Temp. (°C)	Conditions	<u>2</u>	<u>3</u>	<u>4</u>	Ref.
1	<u>7</u>	500-520	empty quartz	55.4	35.2	9.4	this work
2	<u>1</u>	500	packed Pyrex	27	67	6	4
3	<u>1</u>	500	<i>a</i>	46.5	43	10.3	4
4	<u>1</u>	477	gold reactor	30	48	22	2

^a From olefin 5 only, normalized

Although this investigation does not strictly prove that 5 is an intermediate in the pyrolysis of 1, it does show that thermolysis of 5 gives all three required compounds, no more and no less. The ratios of (2+3):4 in experiments 1 and 2 are in excellent agreement, but the correlation is not good for 2:3. However, experiment 3 accepts the surmise⁴ that both 5 and 6 can lead to 3 and factors out the contribution from 6, which cannot be involved in the carbene route. Now we see reasonable agreement between the two routes. Considering the difficulties in comparing different reaction conditions and the greater complexity associated with pyrolysis of 1, we feel that the data are in general agreement.

In summary, we have synthesized one proposed intermediate (5) in the photolysis of 1 and shown that the appropriate products result. Hence the most simple and best-supported rationalization for formation of 2, 3, and 4 from 1 involves classical intramolecular elimination of acetic acid to give bridgehead olefins rather than one of the alternate, more exotic pathways suggested.

REFERENCES AND NOTES

- (1) This work was supported by the National Science Foundation through Grant CHE-77-24625.
- (2) H. Kwart and J. Slutsky, *J. Org. Chem.*, 41, 1429 (1976).
- (3) R. Taylor, *J. Chem. Research* (M), 3526 (1978); (S), 267 (1978).
- (4) B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, 97, 2829 (1975).
- (5) D. J. Martella, M. Jones, Jr., P. v. R. Schleyer, and W. F. Maier, *J. Am. Chem. Soc.*, 101, 7634 (1979).
- (6) B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, 96, 7014 (1974).
- (7) B. L. Adams and P. Kovacic, *J. Org. Chem.*, 39, 3090 (1974).

(Received in USA 16 October 1980)