

## The Synthesis of 2,4-Dehydroadamantane

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INTRAMOLECULAR carbene reactions have been used to form interesting strained ring systems.<sup>1</sup>

We report synthesis of tetracyclo[3,3,1<sup>3</sup>,7,0<sup>2,4</sup>]-decane (III) (we prefer the name 2,4-dehydroadamantane) by intramolecular rearrangement of adamantane carbene (II), using the method of Schechter and co-workers.<sup>2</sup> When the dry lithium salt of the *p*-tosylhydrazone of adamantanone<sup>3</sup> (I) is pyrolyzed at 130–140° for 1 hr., 2,4-dehydroadamantane is formed in yields up to 65%. Adamantane formed concurrently in 5% yield can be readily separated from (III) by preparative g.l.c. using a Lao column at 100°.

The highly volatile hydrocarbon, m.p. 202.5–203.5° gives an i.r. spectrum (KBr disc) showing

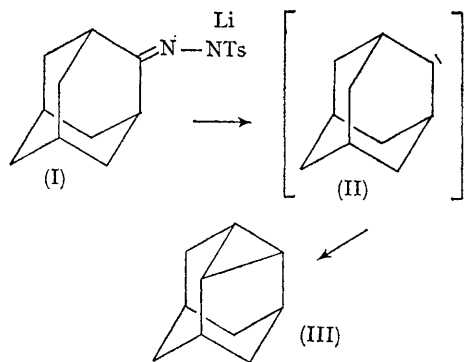
fairly strong absorption at 3030 cm.<sup>-1</sup>, a strong indication of the presence of a cyclopropane ring.<sup>4</sup> Absorptions in the 1030 cm.<sup>-1</sup> region and at 830 cm.<sup>-1</sup>, not present in the infrared spectrum of adamantane, could be ascribed to cyclopropane ring vibrations.<sup>4</sup>

The <sup>1</sup>H n.m.r. spectrum at 60 and 100 Mc./sec. consists of a complex multiplet at  $\tau$  7.6–9.0.

Ring-opening reactions gave further evidence for the structure of (III). Reaction of 2,4-dehydroadamantane with halogen acids<sup>5</sup> in ether gave opening of the cyclopropane ring, furnishing 2-chloro- and 2-bromo-adamantane, identical with authentic samples.<sup>6,7</sup>

Acid-catalyzed acetolysis of (III) (with acetic

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acid containing sulphuric acid) and subsequent hydrolysis of the acetate, gave the known 2-hydroxyadamantane.<sup>3</sup>

Reaction of 2,4-dehydroadamantane (III) with other reagents to furnish disubstituted adamantanes is being investigated.

*Note added in the press:* On the day that this Communication was submitted for publication, a paper was published in *Tetrahedron Letters*, 1966, 4089, by J. E. Baldwin and W. D. Foglesong, describing the synthesis of dehydroadamantanone by another route. The synthesis of 2,4-dehydroadamantane, although mentioned, is not described.

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<sup>2</sup> G. M. Kaufman, J. A. Smith, G. G. Van der Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, 1965, **87**, 935.

<sup>3</sup> P. Schleyer and K. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 182.

<sup>4</sup> H. A. Szymansky, "Interpreted Infrared Spectra," Vol. I, Plenum Press, New York 1964. Although this frequency might also indicate the presence of an olefinic bond, the <sup>1</sup>H n.m.r. spectrum is decisive (and the Bredt rule of course!).

<sup>5</sup> M. Yu. Lukina, *Russ. Chem. Rev.*, 1962, **31**, 419.

<sup>6</sup> W. Hoek, J. Strating, and H. Wynberg, *Rec. Trav. chim.*, 1966, in the press.

<sup>7</sup> G. W. Smith and H. D. Williams, *J. Org. Chem.*, 1961, **26**, 2207.