

Selective Functionalization of Unactivated Methine Positions. 4-Acetyldiamantane

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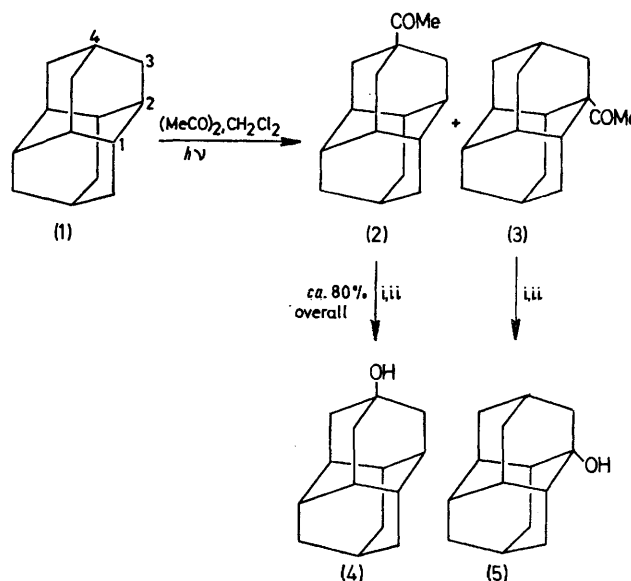
Summary Irradiation of diamantane and biacetyl in methylene chloride gives in 64% yield a mixture of 4-(apical)-acetyl- (2) and 1-(medial)-acetyl-diamantane (3) in 5.5:1 ratio (17:1 after statistical correction); methylene (3-) attack is not observed.

The spectral properties of (2) and (3) were consistent with their structures, definitive proof was obtained by Baeyer-Villiger oxidation⁷ to the known 1- and 4-diamantanols (4) and (5).²

WHILE selective substitution of diamantane (1)¹ at either the 1-(medial)^{2,3} or 3-(secondary) positions² is achieved easily, the same has not been true of 4-(apical) functionalization.²⁻⁴ Two general approaches have been employed. Equilibration of diamantyl halides and alcohols results in only a slight preference for the equatorial-like apical derivatives;²⁻⁴ the 3:1 statistical advantage of the medial position compensates for the steric disadvantage due to its axial character. Insertion of dichloromethylene only exhibits a small (1.8) statistically corrected selectivity for the apical over the medial position.⁵

Photoacetylation, which with adamantane gives exclusively bridgehead substitution in quantitative yield,⁶ seemed like a promising method, especially since the specificity is attributed to steric interaction in the transition state between the biacetyl $n-\pi^*$ triplet and the axial hydrogens of the adamantane methylene groups. In diamantane, such axial interactions would be present not only for secondary, but also for medial positions. We now report that photoacetylation is, indeed, an efficient route for the selective functionalization at the apical position of (1); acetyl products (2) and (3) are obtained in a ratio of ca. 5.5:1. The preference for apical over medial attack is actually 17:1 after statistical correction.

The following result is typical. A solution of diamantane (1.0 g) and biacetyl (20 ml) in CH_2Cl_2 (90 ml) is irradiated in a Pyrex vessel by a high-pressure 100 W mercury lamp under nitrogen for 14 h. After evaporation and chromatography unchanged diamantane (0.64 g), practically pure (2) (0.21 g; 48% yield), m.p. 138.0–138.5° (from $\text{MeOH}-\text{H}_2\text{O}$), and a 1:1 mixture (0.07 g) of (2) and (3) were obtained. Further purification (column chromatography, sublimation, and recrystallization from $\text{MeOH}-\text{H}_2\text{O}$) gave pure (3), m.p. 116.5–117°. The combined yield of (2) and (3) based on consumed diamantane was 64%. Although



Reagents: i, H_2O_2 , HOAc , H^+ ; ii, OH^- , MeOH .

The 4-acetyl derivative (2) obtained by this method provides a convenient starting material for further derivatization of the apical position of diamantane (1).²⁻⁴ The result is also significant because of current interest in the development of methods for the selective attack of methine positions when more than one is present in the same molecule.⁸

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