

SHORT  
COMMUNICATIONS

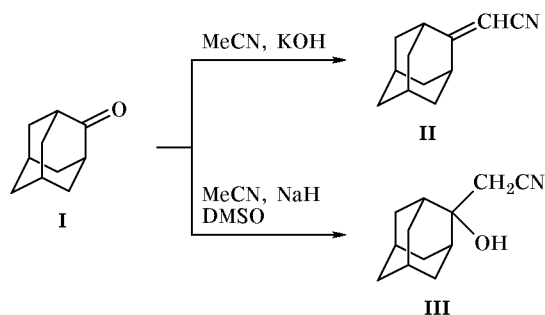
## Reaction of Adamantan-2-one with Acetonitrile in Basic Media

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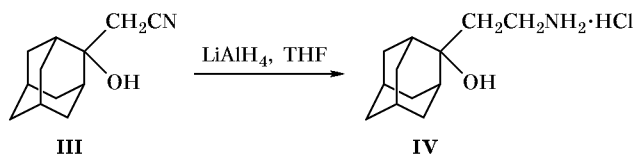
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Substituted acetonitriles containing an activated methylene group are capable of reacting with ketones in the presence of strong bases [1]. We have found that adamantan-2-one (**I**) reacts with acetonitrile in the presence of powdered potassium hydroxide and dicyclohexano-18-crown-6 to give 2-adamantylideneacetonitrile (**II**). Under these conditions, intermediate 2-(2-hydroxy-2-adamantyl)acetonitrile (**III**) readily undergoes dehydration to nitrile **II** which is obtained as the major product (up to 90%, according to the GLC data). The dehydration is favored by elimination of steric strain, which accompanies the transition from the  $sp^3$ -hybridized bridging carbon atom in hydroxy nitrile **III** to  $sp^2$  in **II**. 2-Adamantylideneacetonitrile (**II**) was synthesized previously by the Knoevenagel condensation of adamantan-2-one with cyanoacetic acid [2]. Nitrile **II** characteristically showed in the  $^1\text{H}$  NMR spectrum signals from non-equivalent protons in the bridgehead positions neighboring to the double bond ( $\delta$  2.64 and 3.13 ppm).



The reaction of compound **I** with acetonitrile in dimethyl sulfoxide in the presence of sodium hydride afforded 2-(2-hydroxy-2-adamantyl)acetonitrile (**III**) as the major product. The composition of the reaction mixture (30% of **I** and 70% of **III**, according to the GLC data) did not depend on the molar ratio of sodium hydride and ketone **I**.

Hydroxy nitrile **III** was reduced with lithium tetrahydridoaluminate in tetrahydrofuran. As a result, 2-(2-aminoethyl)-2-hydroxyadamantane was obtained, which was isolated as hydrochloride **IV**.



**2-Adamantylideneacetonitrile (II).** Finely powdered potassium hydroxide, 5 g (0.09 mol), and dicyclohexano-18-crown-6, 0.2 g, in 3 ml of acetonitrile were added to a mixture of 5 g (0.03 mol) of compound **I** in 15 ml of acetonitrile. The mixture was heated under reflux with stirring and poured into water, and the precipitate was filtered off, washed with water, dried, and recrystallized from hexane. Yield 4.5 g (80%), mp 74–75°C; published data [3]: 74.0–74.6°C.  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ - $\text{CCl}_4$ , 1:3),  $\delta$ , ppm: 1.78–2.1 m (12H, Ad), 2.64 s (1H, Ad), 3.13 s (1H, Ad), 5.12 s (1H, CHCN).

**2-(2-Hydroxy-2-adamantyl)acetonitrile (III).** Sodium hydride, 9 g (0.37 mol), was added in small portions with stirring to 150 ml of anhydrous DMSO, and 25 ml of acetonitrile and 6 g (0.04 mol) of compound **I** were added on cooling. The mixture was stirred for 1 h and poured into water, and the precipitate was filtered off, washed with water, dried at a temperature not exceeding 100°C, and recrystallized from ethyl acetate. Yield 3.9 g (60%), mp 140–141°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3433, 2256, 1292, 1172, 1124, 1076, 565.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.56 s (1H, OH), 1.6–2.02 m (12H, Ad), 2.12–2.52 m (2H, Ad), 2.77 s (2H,  $\text{CH}_2\text{CN}$ ). Found, %: C 77.51; H 8.82; N 7.36.  $\text{C}_{12}\text{H}_{17}\text{NO}$ . Calculated, %: C 77.35; H 8.96; N 7.32.

**2-(2-Aminoethyl)-2-hydroxyadamantane hydrochloride (IV).** A solution of 2.6 g (0.02 mol) of compound **III** in 80 ml of tetrahydrofuran was added dropwise with stirring to a suspension of 6.4 g (0.16 mol) of lithium tetrahydridoaluminate in 50 ml of tetrahydrofuran. The mixture was stirred for 1 h, the precipitate was filtered off and washed with THF, and the filtrate was combined with the washings and saturated with dry hydrogen chloride. The precipitate of hydrochloride **IV** was filtered off and dried. Yield 2.5 g (82%), mp 280–283°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3250, 2110, 1615, 1550, 1160, 920, 610.  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 1.45 m (2H, AdCH<sub>2</sub>), 1.65–2.05 m (14H, Ad), 2.27 m (2H, CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), 4.15 s (1H, OH), 8.12 s (3H, NH<sub>3</sub><sup>+</sup>). Found, %:

C 63.06; H 9.12; N 6.39. C<sub>12</sub>H<sub>22</sub>ClNO. Calculated, %: C 62.19; H 9.57; N 6.04.

The IR spectra were recorded on a Shimadzu FTIR-8400S instrument, and the  $^1\text{H}$  NMR spectra were obtained on a Bruker AM-300 spectrometer (300 MHz) using HMDS as internal reference.

#### REFERENCES

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