

SHORT  
COMMUNICATIONS

## Synthesis of Adamantyl-Containing Cyclic $\beta$ -Diketones

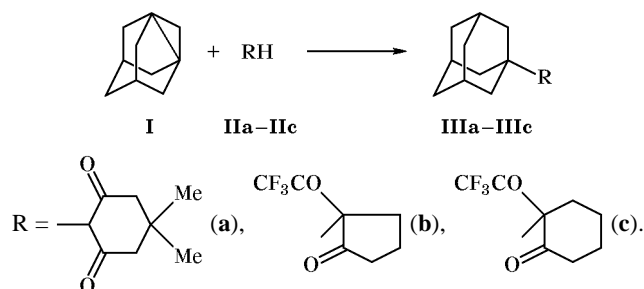
B. I. No<sup>1</sup>, G. M. Butov<sup>1,2</sup>, V. M. Mokhov<sup>1</sup>, and G. Yu. Parshin<sup>1</sup>

<sup>1</sup> Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia

<sup>2</sup> Volga Polytechnical Institute (a Division of VolgGTU)

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We previously reported on the reaction of 1,3-dehydroadamantane (**I**) with aliphatic ketones [1]. While continuing our studies on reactions of 1,3-dehydroadamantane with carbonyl compounds, we were the first to accomplish its reaction with a series of cyclic  $\beta$ -diketones, including those containing a trifluoromethyl group, in the absence of a catalyst:



The reactions were carried out in an inert solvent, diethyl ether, on heating at the boiling point in an atmosphere of dry deoxygenated nitrogen. The molar reactant ratio compound **I**: $\beta$ -diketone was 1:1.5–2, and the reaction time was 1–2 h. With a smaller amount of the initial  $\beta$ -diketone, the conversion of compound **I** was incomplete. The reaction was accompanied by an appreciable exothermic effect, and diketones **IIIa-IIIc** were obtained in 86–98% yield. The products were purified by vacuum distillation, followed by recrystallization from 2-propanol. Their structure was proved by elemental analyses and <sup>1</sup>H and <sup>13</sup>C NMR, IR, and mass spectra.

$\beta$ -Diketones are known [2, 3] to give rise to tautomeric equilibrium in which the enol form prevails. For example, compound **IIa** exists mainly in the enol form ( $pK_a$  5.23 in water) [3]. However, the alkylation occurs exclusively at the carbon atom.

**2-(1-Adamantyl)-5,5-dimethyl-1,3-cyclohexanedione (IIIa)**. Yield 98%, mp 113°C (from isopropyl alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2848–2912 (C–H); 1684 (C=O). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm:

1.05 s (6H, 2CH<sub>3</sub>), 1.63 s (12H, CH<sub>2</sub>, Ad), 2.12 s (3H, CH, Ad), 2.21 s (4H, CH<sub>2</sub>), 2.63 s (1H, CH). Found, %: C 78.68; H 9.35.  $M^+$  274. C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>. Calculated, %: C 78.79; H 9.55.  $M$  274.40.

**2-(1-Adamantyl)-2-trifluoroacetylcyclopentanone (IIIb)**. Yield 86%, mp 46–47°C (from isopropyl alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2860–2928 (C–H); 1692 (C=O). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 1.59 s (12H, CH<sub>2</sub>, Ad), 1.95 s (2H, CH<sub>2</sub>), 2.14 s (3H, CH, Ad), 2.4–2.45 t (2H, CH<sub>2</sub>), 2.68–2.74 t (2H, CH<sub>2</sub>CO). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 314 (1),  $M^+$ , 217 (1) [ $M$ -CF<sub>3</sub>CO]<sup>+</sup>, 135 (100) Ad<sup>+</sup>. Found, %: C 64.85; H 6.68.  $M^+$  314. C<sub>17</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>. Calculated, %: C 64.96; H 6.73.  $M$  314.34.

**2-(1-Adamantyl)-2-trifluoroacetylcyclohexanone (IIIc)**. Yield 93%, mp 104–105°C (from isopropyl alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2860–2928 (C–H); 1692 (C=O). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 1.59 s (12H, CH<sub>2</sub>, Ad), 1.92 s (4H, 2CH<sub>2</sub>), 2.12 s (3H, CH, Ad), 2.27 s (2H, CH<sub>2</sub>), 2.38 s (2H, CH<sub>2</sub>CO). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 328 (2.2)  $M^+$ , 231 (0.8) [ $M$ -CF<sub>3</sub>CO]<sup>+</sup>, 135 (100) Ad<sup>+</sup>. Found, %: C 65.81; H 7.14.  $M^+$  328. C<sub>18</sub>H<sub>23</sub>F<sub>3</sub>O<sub>2</sub>. Calculated, %: C 65.84; H 7.06.  $M$  328.37.

The <sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz). The mass spectra were measured on a Kratos MS-30 instrument. The IR spectra were obtained on a Specord M80 spectrometer in mineral oil.

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