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SHORT COMMUNICATIONS

Synthesis of Adamantyl-substituted Keto Esters

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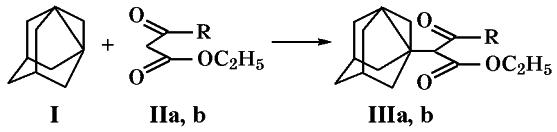
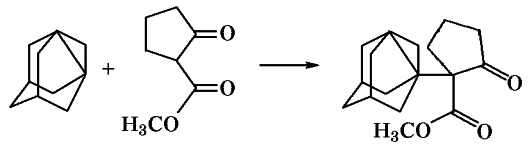
The known adamantyl-substituted ketoesters are widely used in the synthesis of a number of biologically active heterocyclic compounds [1–3]; however the existing preparation procedures provide the target products in low yields [2, 3].

We established formerly that 1,3-dehydroadamantane (**I**) reacted with aliphatic ketones and cyclic β-diketones [4, 5]. In extension of research on 1,3-dehydroadamantane reactions with carbonyl compounds we performed for the first time a reaction between 1,3-dehydroadamantane (**I**) and a series of ketoesters, among which was cyclic methyl 2-oxocyclopentanonecarboxylate (**IIc**).



I **IIa, b** **IIIa, b**

R = CH_3 (**a**), C_6H_4 (**b**).



I **IIc** **IIIc**

The adamantylation of ethyl acetoacetate (**IIa**) in a boiling inert solvent (ethyl ether) under an atmosphere of dry nitrogen purified from oxygen at the molar ratio of reagents **I** and **IIa** equal to 1: 1.5–2 within 1–2 h afforded ethyl 2-(1-adamantyl)-3-oxobutanoate (**IIIa**) in a moderate yield (51%). The target ketoesters **IIIa–c** were obtained in a high yield (83–95%) at longer reaction time (4 h) than that required in the process involving cyclic β-diketones (1–2 h) [5]. We believe that this difference in reactivity is due to lower CH-acidity of ketoesters (**IIa–c**) (pK_a 12–13 [6]) as compared to cyclic β-diketones (pK_a 5–6 [6]).

Compounds **IIIa–c** were purified by vacuum distillation. Compound **IIIc** was additionally recrystallized from 2-propanol. The composition and structure of compounds synthesized were confirmed by ^{1}H NMR and mass spectra, and by elemental analysis.

Ethyl 2-(1-adamantyl)-3-oxobutanoate (IIIa). Yield 83%, bp 180–181 (4 mm Hg), n_D 1.5104. ^{1}H NMR spectrum (DMSO-d_6, 200 MHz), δ, ppm: 1.28 s (3H, CH_3), 1.51 s (12H, CH_2, Ad), 1.9 s (3H, CH, Ad), 2.15 s (3H, CH_3), 3.1 s (1H, CH), 4.1 s (2H, OCH_2). Mass spectrum, I_{rel}, %: 264 (4%) $[M]^+$, 222 (7%) $[M - CH_2CO]^+$, 135 (100%) Ad^+. Found, %: C 73.12; H 9.31. *M* 264.12. $C_{16}H_{24}O_3$. Calculated, %: C 72.69; H 9.15. *M* 264.36.

Ethyl 3-adamantyl-3-phenyl-3-oxopropanoate (IIIb). Yield 90%, bp 217–218 (1 mm Hg), n_D 1.5580. ^{1}H NMR spectrum (DMSO-d_6, 200 MHz), δ, ppm: 1.28 s (3H, CH_3), 1.60 s (12H, CH_2, Ad), 1.88 s (3H, CH, Ad), 3.84 s (2H, CH, OCH_2), 4.16 s (1H, CH), 7.18–7.48 m (4H, CH, Ph), 7.82–7.96 m (1H, Ph). Mass spectrum, I_{rel}, %): 326 (6%) $[M]^+$, 135 (28%) Ad^+, 105 (100%) $PhCO^+$, 77 (40%) Ph^+. Found, %: C 77.68; H 8.12. *M* 326.15. $C_{21}H_{26}O_3$. Calculated, %: C 77.27; H 8.03. *M* 326.43.

Methyl 1-(1-adamantyl)-2-oxocyclopentanecarboxylate (IIIc). Yield 95%, bp 171–172 (1 mm Hg), mp 41–42°C (from 2-propanol). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: C 1.28 s (3H, CH_3), 1.55 s (12H, CH2, Ad), 2.0 s (3H, CH, Ad), 1.9 s (2H, CH, CH_2), 2.05 (2H, CH, CH_2), 2.15 s (2H, CH, CH_2), 3.6 s (3H, CH, CH_3). Found, %: C 74.05; H 9.70. *M* 276.34. $C_{17}H_{24}O_3$. Calculated, %: C 73.93; H 9.65. *M* 276.17.

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^{1}H NMR spectra were registered on spectrometers Bruker AC-200 (200 MHz) and Bruker AM-300 (300 MHz). Mass spectra were taken on Kratos MS-30 instrument.

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