Russian Journal of Organic Chemistry, Vol. 37, No. 12, 2001, pp. 1791–1792. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 12, 2001, pp. 1872–1873.
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SHORT COMMUNICATIONS

Reactions of CH Acids with α,β-Unsaturated Ketones of the Adamantane Series

A. A. Pimenov, N. V. Makarova, I. K. Moiseev, and M. N. Zemtsova

Samara State Technical University, Galaktionovskaya 141, Samara, 443010 Russia
tel. (846) 322 122; fax: (846) 322 122; e-mail: moiseev@dp.sstu.samara.ru

Received February 2, 2001

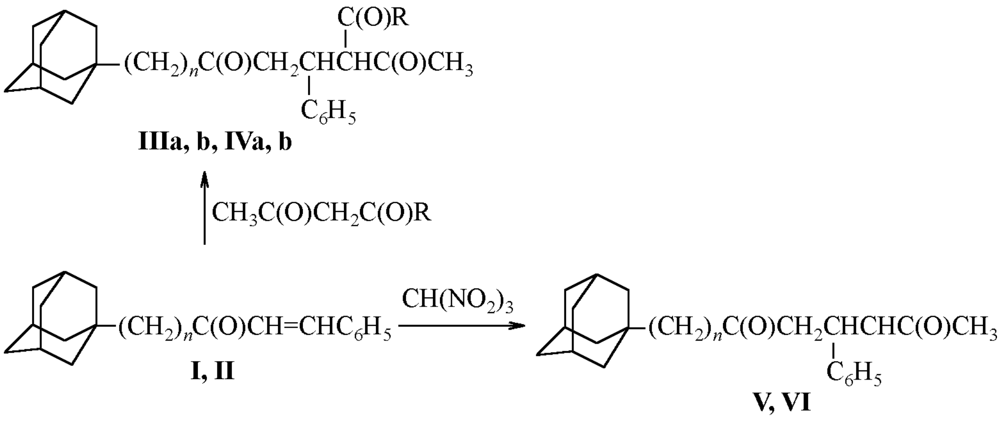
According to published data, aromatic α,β-unsaturated ketones react with CH acids, generally following the 1,4-addition pattern [1–5]. However, apart from 1,2- and 1,4-addition, these reactions can be accompanied by cyclization or cycloisomerization of the 1,4-adducts. For example, 1,3-diphenyl-2-propen-1-one reacts with ethyl acetoacetate and its derivatives to give ethyl 2-oxo-4,6-diphenyl-3-cyclohexenecarboxylate and its substituted analogs [6].

In continuation of our studies on α,β-unsaturated ketones of the adamantane series [7] and with the goal of obtaining new adamantyl-containing ketones, we examined the reactions of 1-(1-adamantyl)-3-phenyl-2-propenone (**I**) and 1-(1-adamantyl)-4-phenyl-3-buten-2-one (**II**) with the following CH acids: acetylacetone, ethyl acetoacetate, and trinitromethane. The reactions were carried out in anhydrous ethanol using 10% sodium ethoxide as a base which is incapable of forming complexes at the carbonyl oxygen atom of ketones **I** and **II**. The reactant mixtures were refluxed for 5–7 h. As a result, we obtained 4-acetyl-1-(1-adamantyl)-3-phenylhexane-1,5-dione (**IIIa**), 5-acetyl-1-(1-adamantyl)-4-phenylheptane-2,6-dione (**IVa**), 1-(1-adamantyl)-4-(ethoxycarbonyl)-3-phenylhexane-1,5-dione (**IIIb**), and 1-(1-adamantyl)-5-(ethoxycarbonyl)-4-phenylheptane-2,6-dione (**IVb**). The reactions of **I** and **II** with trinitromethane in dioxane at room temperature in the absence of a catalyst afforded 1-(1-adamantyl)-4,4,4-trinitro-3-phenyl-1-butanone (**V**) and 1-(1-adamantyl)-5,5,5-trinitro-4-phenyl-2-pentanone (**VI**), respectively (Scheme 1).

According to the ^{1}H NMR data, compounds **III–VI** are 1,4-addition products of CH acids at the double bond of unsaturated ketones **I** and **II**. No cyclization of the adducts was observed.

4-Acetyl-1-(1-adamantyl)-3-phenyhexane-1,5-dione (IIIa). Ketone **I**, 3.8 mmol, and freshly distilled acetylacetone, 3.8 mmol, were dissolved on heating

Scheme 1.



R = CH$_3$ (**a**), R = C$_2$H$_5$O (**b**); **I**, **III**, **V**, n = 0; **II**, **IV**, **VI**, n = 1.

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in 20 ml of a 10% solution of sodium ethoxide in anhydrous ethanol. The mixture was refluxed for 7 h and diluted with 100 ml of water, and the precipitate was filtered off, dried, and recrystallized from hexane. Yield 63%, mp 111–113°C. ^{1}H NMR spectrum, δ, ppm: 1.65–1.96 m (15H, CH_2 and CH in Ad), 2.42 s (6H, CH_3CO), 3.22 d (2H, $COCH_2$), 3.79 q (1H, $C\mathbf{H}C_6H_5$), 5.76 d (1H, CH), 6.80–7.30 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1715, 1705 (C=O).

1-(1-Adamantyl)-4-(ethoxycarbonyl)-3-phenylhexane-1,5-dione (IIIb) was synthesized in a similar way. Yield 49%, mp 108–109°C. ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, $CH_2C\mathbf{H}_3$), 1.65–1.96 m (15H, CH_2 and CH in Ad), 2.41 s (3H, CH_3CO), 2.76 d (2H, $COCH_2$), 3.05 q (1H, $C\mathbf{H}C_6H_5$), 3.22 q (2H, $C\mathbf{H}_2CH_3$), 5.75 d (1H, CH), 6.95–7.30 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1745, 1735, 1715 (C=O).

5-Acetyl-1-(1-adamantyl)-4-phenylheptane-2,6-dione (IVa) was synthesized in a similar way. Yield 71%, mp 148–150°C. ^{1}H NMR spectrum, δ, ppm: 1.20 s (6H, CH_3CO), 1.75–1.98 m (15H, CH_2 and CH in Ad), 2.58 s (2H, CH_2, Ad), 3.24 d (2H, $COCH_2$), 4.14 q (1H, $C\mathbf{H}C_6H_5$), 5.78 d (1H, CH), 6.80–7.20 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1730, 1710 (C=O).

1-(1-Adamantyl)-5-(ethoxycarbonyl)-4-phenylheptane-2,6-dione (IVb) was synthesized in a similar way. Yield 61%, mp 138–140°C. ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, $CH_2C\mathbf{H}_3$), 1.68–1.96 m (15H, CH_2 and CH in Ad), 2.27 s (2H, $AdCH_2$), 2.53 s (3H, CH_3CO), 3.17 d (2H, $COCH_2$), 3.25 q (1H, $C\mathbf{H}C_6H_5$), 3.49 q (2H, $C\mathbf{H}_2CH_3$), 5.77 d (1H, CH), 7.48–7.83 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1755, 1720, 1705 (C=O).

1-(1-Adamantyl)-4,4,4-trinitro-3-phenyl-2-butanone (V). Ketone **I**, 3.8 mmol, and trinitromethane, 0.57 g (3.8 mmol), were dissolved in 8 ml of dioxane, and the mixture was kept for 12 h at room temperature. It was then diluted with 100 ml of water, and the product was filtered off and recrystallized from ethanol. Yield 81%, mp 131–132°C. ^{1}H NMR spectrum, δ, ppm: 1.65–1.93 m (15H, CH_2 and CH in Ad), 3.22 d (2H, $COCH_2$), 5.76 d (1H, CH), 7.42–7.97 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1725 (C=O); 1670, 1345 (NO_2).

1-(1-Adamantyl)-5,5,5-trinitro-4-phenyl-2-pentanone (VI) was synthesized in a similar way. Yield 93%, mp 84–86°C. ^{1}H NMR spectrum, δ, ppm: 1.58– 1.85 m (15H, CH_2 and CH, Ad), 2.14 s (2H, $AdCH_2$), 3.43 d (2H, $COCH_2$), 5.24 d (1H, CH), 7.36–7.79 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2, Ad); 1720 (C=O); 1630, 1320 (NO_2).

The ^{1}H NMR spectra were recorded on a Bruker AC-300 instrument (300.13 MHz) in DMSO relative to HMDS as internal reference. The IR spectra were measured on a Specord M-80 spectrometer in KBr. The purity of the products was checked by thin-layer chromatography on Silufol UV-254 plates (development with iodine vapor).

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