ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 4, pp. 608–609. © Pleiades Publishing, Ltd., 2010.
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SHORT COMMUNICATIONS

Synthesis of Nitroso- and Aminopyrazoles Containing an Adamantane Fragment

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Received June 25, 2009

DOI: 10.1134/S1070428010040342

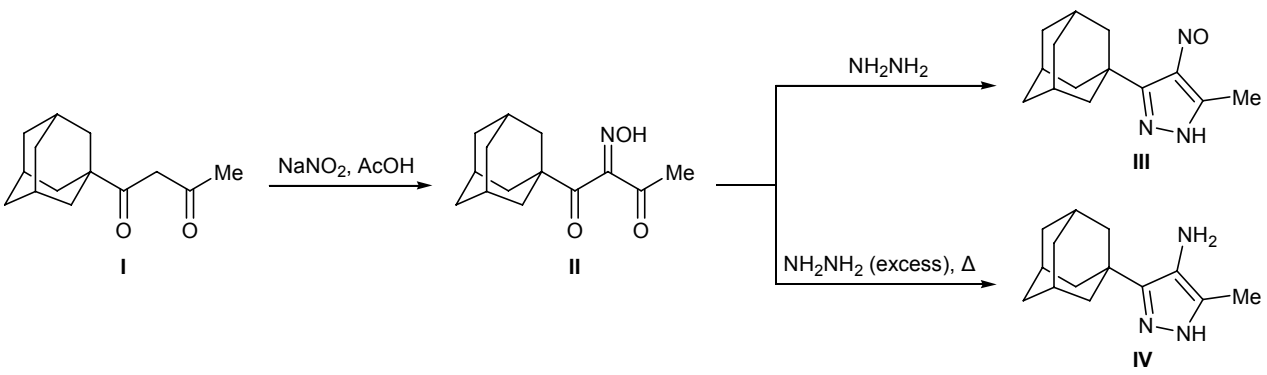
In the recent years, chemistry of nitrogen-containing heterocyclic compounds attracts researchers' attention due to their practical importance and biological activity. On the other hand, a number of effective medicines with different kinds of activity contain an adamantane fragment as pharmacophoric group. The synthesis of pyrazoles having an adamantane fragment was described in [1–3]. The goal of the present work was to synthesize adamantane-containing nitroso- and aminopyrazoles.

For this purpose, 1-(1-adamantyl)butane-1,3-dione (**I**) was treated with sodium nitrite in acetic acid to obtain 1-(1-adamantyl)butane-1,2,3-trione 2-oxime (**II**). Oxime **II** reacted with an equimolar amount of hydrazine at room temperature to give 3-(1-adamantyl)-5-methyl-4-nitroso-1*H*-pyrazole (**III**). By heating oxime **II** with excess hydrazine we obtained 3-(1-adamantyl)-5-methyl-1*H*-pyrazol-4-amine (**IV**).

1-(1-Adamantyl)butane-1,3-dione (**I**) was synthesized according to the procedure described in [4].

1-(1-Adamantyl)butane-1,2,3-trione 2-oxime (II). A solution of 0.94 g (13.6 mmol) of sodium nitrite in 2 ml of water was added dropwise under stirring and cooling over a period of 15 min to a solution of 1.5 g (6.8 mmol) of diketone **I** in 12 ml of glacial acetic acid, maintaining the temperature below 15°C. The mixture was then stirred for 3 h at 25°C, poured into 200 ml of ice water, and extracted with chloroform (3×100 ml). The organic extracts were combined and dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from petroleum ether (bp 40–70°C). Yield 1.1 g (65%), yellow crystals, mp 138–141°C. IR spectrum, ν, cm^{-1}: 3356 (OH); 2904, 2849 (C−H_{Ad}); 1713, 1674 (C=O); 987 (N−O). ^{1}H NMR spectrum, δ, ppm: 1.67–1.98 m (15H, Ad), 2.01 s (3H, CH_3), 12.80 s (1H, OH). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (6) $[M]^+$, 163 (3.5), 135 (100), 107 (19.3), 93 (49.8), 79 (31.6), 67 (13.4), 55 (9), 43 (28.5). Found, %: C 67.51; H 7.75; N 5.71. $C_{14}H_{19}NO_3$. Calculated, %: C 67.47; N 7.63; N 5.62. *M* 249.31.

3-(1-Adamantyl)-5-methyl-4-nitroso-1*H*-pyrazole (III). Hydrazine, 0.04 g (0.8 mmol), was added dropwise on cooling to a solution of 0.2 g (0.8 mmol) of compound **II** in 5 ml of ethanol, and the mixture was kept for 2 h at room temperature; the solution turned dark green. The green precipitate was filtered



off and recrystallized from ethanol. Yield 0.15 g (77%), light green crystals, mp 237–238°C. IR spectrum, ν, cm^{-1}: 3202 (N−H); 2908, 2851 (C−H_{Ad}); 1578 (N=O). ^{1}H NMR spectrum, δ, ppm: 1.70–2.10 m (15H, Ad), 2.28 s (3H, CH_3), 13.10 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 245 (59.6) $[M]^+$, 228 (40.7), 135 (100), 107 (19.3), 93 (49.8), 79 (31.6), 67 (13.4), 55 (9), 43 (28.5). Found, %: C 67.51; H 7.75; N 5.71. $C_{14}H_{19}N_3O$. Calculated, %: C 67.47; H 7.63; N 5.62. *M* 245.32.

3-(1-Adamantyl)-5-methyl-1*H*-pyrazol-4-amine (IV). Hydrazine, 0.16 g (3.2 mmol), was added dropwise on cooling to a solution of 0.2 g (0.8 mmol) of compound **II** in 5 ml of ethanol, and the mixture was heated for 3 h under reflux; the mixture turned first dark green and then became colorless. It was cooled and diluted with 20 ml of water, and the precipitate was filtered off, dried, and recrystallized from ethanol. Yield 0.10 g (54%), colorless crystals, mp 242–245°C. IR spectrum, ν, cm^{-1}: 3221 (NH, NH_2); 2901, 2847 (C−H_{Ad}). ^{1}H NMR spectrum, δ, ppm: 1.25–2.02 m (15H, Ad), 2.10 s (3H, CH_3), 11.08 br.s (3H, NH, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 231 (100) $[M]^+$, 216 (11), 174 (40.3), 157 (11.1), 135 (12.4), 110 (6.5), 93 (9.6), 79 (11), 41 (16.1). Found, %: C 72.50; H 8.91; N 18.01. $C_{14}H_{21}N_3$. Calculated, %: C 72.73; H 9.09; N 18.18. *M* 231.34.

The IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer from samples pelleted with KBr. The ^{1}H NMR spectra were measured on a Bruker AM 300 instrument (300 MHz) using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra were obtained on a Finnigan Trace DCQ mass spectrometer. The elemental compositions were determined on a TermoFinnigan Flash1112 NCH analyzer. The purity of the isolated compounds was checked by TLC on Silufol plates using carbon tetrachloride–acetone (10 : 1, by volume) as eluent.

This study was performed under financial support by the Ministry of Education and Science of the Russian Federation (federal target program "Scientific and Scientific–Pedagogical Personnel of Innovation Russia," project no. NK-262P/5).

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