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SHORT COMMUNICATIONS

Synthesis of α,β-Unsaturated Ketones on the Basis of Bicyclo[3.3.1]nonane-2,6-dione

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

Samara State Technical University, ul. Galaktionovskaya 141, Samara, 443010 Russia
e-mail: moiseev@dp.sstu.samara.ru

Nayanova Samara Municipal University, Samara, Russia

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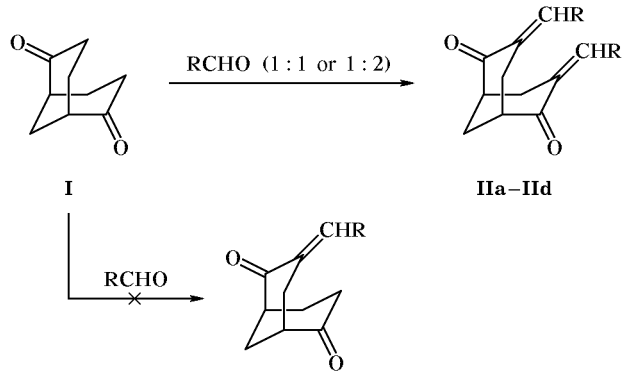
α,β-Unsaturated ketones are widely used in organic chemistry for preparation of both aliphatic [1] and a large number of heterocyclic compounds [2]. Kozlov *et al.* [3] reported on the synthesis of unsaturated ketones by the Claisen–Schmidt reaction of methyl 1-adamantyl ketone. We extended this procedure to (1-adamantyl)acetone and obtained 4-(1-adamantyl)-1-R-1-buten-3-ones [4]. In continuation of our studies on the synthesis of cage-like unsaturated ketones, we examined reactions of bicyclo[3.3.1]nonane-2,6-dione (**I**) with aromatic and heterocyclic aldehydes: benzaldehyde, 4-nitrobenzaldehyde, 2-furaldehyde, and 2-thiophenecarbaldehyde. As a result, the corresponding 3,7-bis(arylmethylene)bicyclo[3.3.1]nonane-2,6-diones **II** were obtained.



R = C_6H_5 (**a**), 4-$NO_2C_6H_4$ (**b**), 2-furyl (**c**), 2-thienyl (**d**).

The reactions were carried out in ethanol at 60–65°C in the presence of potassium hydroxide; the ketone **I**-to-aldehyde ratio was 1 : 2. The reactant ratio did not affect the reaction direction: only bis(arylmethylene) derivatives **II** were obtained regardless of whether the reactant ratio was 1 : 1 or 1 : 2. We failed to isolate monosubstituted ketones.

3,7-Dibenzylidenebicyclo[3.3.1]nonane-2,6-dione (IIa). A mixture of 1.54 g (10 mmol) of bicyclo-[3.3.1]nonane-2,6-dione (**I**), 11 mmol of benzaldehyde, and 10 ml of ethanol was heated to 60–65°C, and a solution of 0.56 g (10 mmol) of potassium hydroxide in 10 ml of ethanol, heated to 60–65°C, was added. After 10 min, the mixture was diluted with 100 ml of water and was left to stand for 24 h. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 51%. mp 194–196°C. IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2); 1695 (C=O). ^1H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 2.50 m (6H, $3CH_2$), 2.90 m (2H, 2CH), 6.50 s (1H, CH=), 6.70–7.30 m (10H, $2C_6H_5$).

3,7-Bis(*p*-nitrobenzylidene)bicyclo[3.3.1]nonane-2,6-dione (IIb) was synthesized in a similar way. Yield 76%. mp 267–269°C. IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2); 1680 (C=O). ^1H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 2.50 m (6H, $3CH_2$), 3.55 m (2H, 2CH), 7.38 s (1H, CH=), 7.70–8.25 m (8H, $2C_6H_4$).

3,7-Difurfurylidenebicyclo[3.3.1]nonane-2,6-dione (IIc) was synthesized in a similar way. Yield 62%. mp 153–155°C. IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2); 1685 (C=O). ^1H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 2.30 m (6H, $3CH_2$), 2.50 m (2H, 2CH), 6.70 s (1H, CH=), 7.18–7.95 m (6H, CH, furan).

3,7-Dithenylidenebicyclo[3.3.1]nonane-2,6-dione (IId) was synthesized in a similar way. Yield 56%.

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mp 247–249°C. IR spectrum, ν, cm^{-1}: 2900, 2850 (CH_2); 1670 (C=O). ^1H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 2.45 m (6H, $3CH_2$), 3.05 m (2H, 2CH), 7.75 s (1H, CH=), 7.20–7.90 m (6H, CH, thiophene).

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