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SHORT COMMUNICATIONS

New Route of Reaction between Acyl Isothiocyanates and Cyclic β-Diketones

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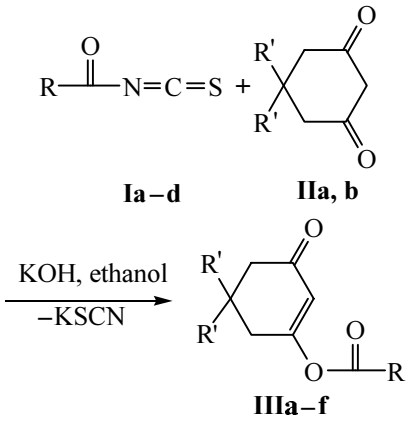
The reaction of acyl isothiocyanates with β-dicarbonyl compounds is thoroughly studied nowadays [1–10]. In a wide range of reaction conditions the process proceeds as C-thiocarbamoylation of the dicarbonyl component. For instance, C-thiocarbamoylated derivatives of 1,3-cyclohexanedione [7] or dimedone [8, 9] formed in good yields at boiling reagents in dioxane or acetone.

We found reaction conditions where the character of the process crucially changed: the acyl isothiocyanates operated not as thiocarbamoylating but as acylating agents. It was demonstrated that reaction of benzoyl isothiocyanates **Ia**–**Id** with cyclic diketones **IIa, IIb** in the presence of equimolar amount of KOH at room temperature furnished O-acylation products **IIIa**–**IIIf**.

We assume as more probable a direct O-acylation of β-diketones of **II** type with compounds **I** whose isothiocyanate group under the reaction conditions



Ia–d **IIa, b** **IIIa–f**

I, R = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**); **II**, R' = H (**a**), Me (b); **III**, R' = H, R = Ph (**a**), 4-ClC_6H_4 (**b**), R' = Me, R = Ph (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**).

(alcohol solution of KOH) acts as pseudohaloid. We believe that conversion of C-carbamoylated products into O-acylated derivatives under the action of alkali is less probable. The latter is confirmed by formation of derivatives of S,N-ketene acetal type in reaction between benzoyl isothiocyanate with β-dicarbonyl compounds in DMF in the presence of KOH [3].

Compounds **IIIa–IIIf** are viscous oily fluids. Their struc-ture was confirmed by IR spectra containing characteristic absorption bands of keto (1665–1675 cm^{-1}) and ester (1725–1740 cm^{-1}) carbonyl groups, and by ^1H NMR spectra where appeared a signal from proton CH= at 5.94–6.06 ppm

3-Acyloxy-2-cyclohexen-1-ones (IIIa–IIIf). To a solution of 0.006 mol of β-diketone **IIa, IIb** and 0.337 g (0.006 mol) of KOH in 30 ml of ethanol was added at stirring in one portion 0.006 mol of benzoyl isothiocyanate **Ia–d**. After stirring for 15 min the reaction mixture was poured into water (50 ml), the organic products were extracted into dichloromethane (2×25 ml), the extract was dried on Na_2SO_4, and the solvent was evaporated. Then the residue was extracted with boiling hexane (100 ml), and on evaporating the solvent the substance was subjected to chromatography (eluent ethylacetate–hexane, 1:2).

3-Benzoyloxy-2-cyclohexen-1-one (IIIa). Yield 76%, R_f 0.82. IR spectrum, cm^{-1}: 1675, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 2.07–2.11m (2H, H^5), 2.38–2.41m (2H, H^6), 2.70–74m (2H, H^4), 5.91s (1H, CH=), 7.59–7.73m (3H, $H^{3'}$, $H^{4'}$, $H^{5'}$), 8.09d (2H, $H^{2'}$, $H^{6'}$, J 7.8 Hz). Found, %: C 71.83; H 5.72. $C_{13}H_{12}O_3$. Calculated, %: C 72.21; H 5.59.

3-(4-Chlorobenzoyloxy)-2-cyclohexen-1-one (IIIb). Yield 61%, R_f 0.60. IR spectrum, cm^{-1}: 1675, 1735

(C=O). ^{1}H NMR spectrum, δ, ppm: 2.10–2.14 m (2H, H^5), 2.46 t (2H, H^6, *J* 5.8 Hz), 2.67 t (2H, H^4, *J* 5.8 Hz), 6.04 c (1H, CH=), 7.47 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.0 Hz), 8.02 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.0 Hz). Found, %: C 62.59; H 4.30. $C_{13}H_{11}ClO_3$. Calculated, %: C 62.29; H 4.42.

3-Benzoyloxy-5,5-dimethyl-2-cyclohexen-1-one (IIIc). Yield 72%. R_f 0.71. IR spectrum, cm^{-1}: 1670, 1725 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.16 s (6H, 2Me), 2.33 s (2H, H^6), 2.56 s (2H, H^4), 6.06 s (1H, CH=), 7.50–7.53 m (2H, $H^{3'}$, $H^{5'}$), 7.65 t (1H, $H^{4'}$, *J* 7.8 Hz), 8.08 d (2H, $H^{2'}$, $H^{6'}$, *J* 7.7 Hz). Found, %: C 74.07; H 6.77. $C_{15}H_{16}O_3$. Calculated, %: C 73.75; H 6.60.

3-(4-Chlorobenzoyloxy)-5,5-dimethylcyclohexen-1-one (IIId). Yield 63%, R_f 0.74. IR spectrum, cm^{-1}: 1665, 1730 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.16 s (6H, 2Me), 2.33 s (2H, 4-CH_2), 2.55 s (2H, H^4), 6.05 s (1H, CH=), 7.47 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.0 Hz), 8.02 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.0 Hz) Found, %: C 64.52; H 5.60. $C_{15}H_{15}ClO_3$. Calculated, %: C 64.64; H 5.42.

3-(4-Bromobenzoyloxy)-5,5-dimethyl-2-cyclohexen-1-one (IIIe). Yield 60%, R_f 0.8. IR spectrum, cm^{-1}: 1670, 1725 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.16 s (6H, 2Me), 2.34 s (2H, H^6), 2.55 s (2H, H^4), 6.05 s (1H, CH=), 7.64 d (2H, $H^{3'}$, $H^{5'}$, *J* 7.8 Hz), 7.93 d (2H, $H^{2'}$, $H^{6'}$, *J* 7.8 Hz) Found, %: C 55.98; H 4.86. $C_{15}H_{15}BrO_3$. Calculated, %: C 55.75; H 4.68.

3-(4-Methoxybenzoyloxy)-5,5-dimethyl-2-cyclohexen-1-one (IIIf). Yield 65%, R_f 0.70. IR spectrum, cm^{-1}: 1665, 1740 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.15 s (6H, 2Me), 2.33 s (2H, H^6), 2.53 s (2H, H^4), 6.04 s (1H, CH=), 6.97 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.0 Hz), 8.03 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.0 Hz) Found, %: C 69.73; H 6.47. $C_{16}H_{18}O_4$. Calculated, %: C 70.06; H 6.61.

IR spectra were recorded on spectrophotometer UR-20 from solutions in CH_2Cl_2. ^{1}H NMR spectra were registered on spectrometer Varian-Gemini (300.0 MHz) in $CDCl_3$, internal reference TMS.

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