

LETTERS
TO THE EDITOR

Features of the Reaction of Some Symmetrically Substituted Isoindigos with Hydrazine Hydrate

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Abstract—Depending on the structure of the substituent at the nitrogen atom of the heterocycle, reaction of isoindigo derivatives with hydrazine hydrate leads to the formation of either oxindole derivatives, or to a substituted isatin-3-hydrazone.

Keywords: oxindole, isoindigo, reductive cleavage

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Reaction of α,β -unsaturated carbonyl compounds with hydrazine is widely used in the synthesis of 1*H*-pyrazoles [1–3]. In recent years new aspects of the reaction of hydrazine with alkenes containing carbonyl fragments are revealed. For example, the reaction of hydrazine hydrate with a wide range of alkenes under heating in an alcoholic solution resulted in a reduction of the double bond [4]. In addition, when performing this reaction at room temperature in the presence of guanidine nitrate, the endocyclic C=C bonds can also be subject to the reduction process [5]. In all cases the double bond rupture was not observed. It should also be noted that we have not been able to find reports on the involvement of compounds containing a double carbon–carbon bond conjugated with two carbonyl groups into similar reactions. One of such objects is isoindigo and its derivatives, which has been of special interest in the last decade [6–9].

Previously we have shown that isoindigo derivatives undergo a reductive cleavage of the C=C bond under the action of hydrazine hydrate [10]. In order to identify the features of this reaction we studied the reactions with hydrazine hydrate of symmetrically substituted isoindigo **1–3** [11, 12] containing alkyl or *p*-methylbenzyl substituents. The reactions proceeded in ethanol with a large excess of hydrazine for 10–15 min, they began already at 30°C and completely terminated at 45°C. As the reaction completed, dark red color of the reaction mixture disappeared, indicat-

ing an interruption of the conjugation of C(O)–C=C–C(O) chain in the isoindigo molecule.

The structure of the reaction products was confirmed by ¹H and ¹³C NMR spectroscopy data. Thus, in the ¹H NMR spectrum of compounds **4** and **5** no signals were observed in the range of 9.0–9.2 ppm, which is characteristic of the proton H⁴ of isoindigo derivatives. At the same time, in the upfield region signals of the alkyl protons were registered, as well as the signal of the methylene protons of the five-membered ring (3.5 ppm, 2H). Due to the low solubility of 1,1'-bis(*p*-methylbenzyl)isoindigo **3** in ethanol its reaction with an excess of hydrazine was carried out under reflux conditions. As a result the 1-(4-methylbenzyl)isatin-3-hydrazone **6** was obtained in a nearly quantitative yield. In the IR spectrum of **6** absorption bands of the stretching vibrations of the =N–NH₂ fragment (ν 3365, 3210 and 3155 cm⁻¹) were observed. The ¹H NMR spectrum contained a broadened signal at 10.6 ppm belonging to the protons of NH₂ group. The mass spectrum of **6** contained the peak of the molecular ion of *m/z* 265.1.

General procedure for the preparation of compounds 4 and 5. Hydrazine hydrate (3 mL) was added dropwise to a slurry of isoindigo derivative **1** or **2** (0.2 mmol) in 3 mL of 96% ethanol with stirring at room temperature. During the addition, the solution acquired an emerald color. The reaction mixture was heated at 45°C for 5 min. After cooling to room