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SHORT COMMUNICATIONS

Acid Hydrolysis of 3-Aryl-5-trinitromethyl-1,2,4-oxadiazoles

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3,5-Diphenyl-1,2,4-oxadiazole is known to be stable under conditions of acid hydrolysis [1]. The reaction of 5-trinitromethyl-3-phenyl-1,2,4-oxadiazole (**I**) with dilute (1:1) hydrochloric acid resulted in formation of benzamide oxime (**V**) via decomposition of the oxadiazole ring. Attempted selective hydrolysis of trinitromethyl group in **I** under mild conditions (acetic acid) afforded 5-hydroxy-3-phenyl-1,2,4-oxadiazole (**III**) (Scheme 1).

The acid hydrolysis of 3-(4-tolyl)-5-trinitromethyl-1,2,4-oxadiazole (**II**) takes a similar pathway. It is reasonable to presume that 5-hydroxy derivatives **III** and **IV** are formed as intermediates when the acid hydrolysis of **I** and **II** is performed under more severe conditions. In fact, heating of 5-hydroxy-3-phenyl-1,2,4-oxadiazole (**III**) in boiling dilute hydrochloric acid gave benzamide oxime (**V**). It is quite probable that the reaction involves elimination of the trinitromethyl group from oxadiazoles **I** and **II** to give compounds **III** and **IV**; the latter are then converted into benzamide oximes **V** and **IV**.

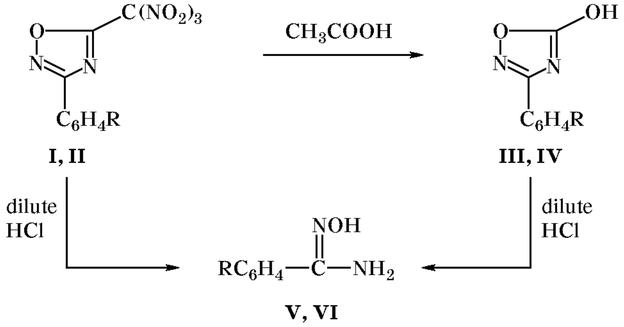
Compounds **I** and **II** were synthesized by the procedure described in [2].

Hydrolysis of 3-aryl-5-trinitromethyl-1,2,4-oxadiazoles I and II in acetic acid. A mixture of 5 mmol of compound **I** or **II**, 50 ml of acetic acid, and 10 ml of water was refluxed for 1 h. The solution was evaporated, and the residue was subjected to column chromatography (10 × 250-mm column) on activated silica gel (Silicagel 100/400 μm) using diethyl ether as eluent. We isolated 0.5 g (63%) of 5-hydroxy-3-phenyl-1,2,4-oxadiazole (**III**), mp 203°C [3], or 0.6 g (68%) of 5-hydroxy-3-(4-tolyl)-1,2,4-oxadiazole (**IV**), mp 220°C [4].

Hydrolysis of 3-aryl-5-trinitromethyl-1,2,4-oxadiazoles I and II in hydrochloric acid. A mixture of 3 mmol of compound **I** or **II**, 30 ml of concentrated hydrochloric acid, and 10 ml of water was refluxed for 3 h. The solution was evaporated, and the residue was purified by column chromatography (see above) with benzene as eluent. We isolated 0.2 g (53%) of benzamide oxime (**V**), mp 78–80°C [5], or 0.3 g (61%) of 4-methylbenzamide oxime (**VI**), mp 147°C [6].

Hydrolysis of 3-aryl-5-hydroxy-1,2,4-oxadiazoles III and IV in hydrochloric acid. A mixture of 3 mmol of compound **III** or **IV**, 15 ml of concentrated hydrochloric acid, and 5 ml of water was refluxed for 2.5 h. The solution was evaporated, and the residue was purified by column chromatography (see above) with benzene as eluent. We isolated 0.15 g (35%) of

Scheme 1.



I, **III**, **V**, R = H; **II**, **IV**, **VI**, R = 4-CH_3.

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compound **V**, mp 78–80°C, or 0.1 g (30%) of **VI**, mp 146–147°C.

Compounds **III**–**VI** showed no depression of the melting point on mixing with authentic samples.

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