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SHORT COMMUNICATIONS

Formation of Oxadiazolones in the Oxidative Hydrolysis of Alkylsulfanyl-1,3,4-oxadiazoles

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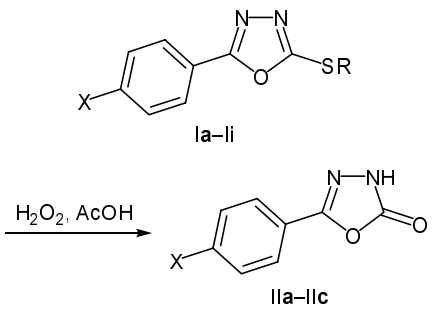
Although the chemistry of oxadiazolones has been studied in sufficient detail [1–4], methods for preparation of these compounds include many steps and are fairly laborious. Taking into account strong biological activity of oxadiazolone derivatives [1, 5], search for simpler procedures for their synthesis is important.

We propose a convenient procedure for the synthesis of 2-aryloxadiazolones via oxidation of the corresponding alkylsulfanyloxadiazoles (Scheme 1). The reactions were carried out according to the standard procedure [6] using 3 equiv of 35% hydrogen peroxide. The products were sufficiently pure, and no additional purification was necessary. The yields were quantitative. The structure of aryloxadiazolones **IIa**–**IIc** was proved by the ^{1}H NMR and mass spectra. In the mass spectra of **IIa**–**IIc**, the most characteristic were the following fragment ion peaks: $[M - CO_2]^{+\cdot}$, $[ArC{\equiv}O]^+$, $[ArC{\equiv}N]^{+\cdot}$, and $[M - CO - HCN]^{+\cdot}$. The fragmentation scheme was proposed on the basis of the data reported in [7, 8].

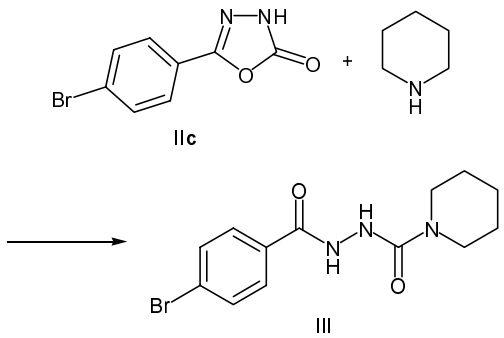
Scheme 1.



I, R = CH_2=$CHCH_2$, X = H (**a**), Me (**b**), Br (**c**); R = $HC{\equiv}C\ CH_2$, X = H (**d**), Me (**e**), Br (**f**); R = $HOCH_2C{\equiv}CCH_2$, X = H (**g**), Me (**h**), Br (**i**); **II**, X = H (**a**), Me (**b**), Br (**c**).

Treatment of compounds **IIa**–**IIc** with secondary amines leads to opening of the oxadiazole ring. For example, the reaction of **IIc** with piperidine in boiling ethanol (4 h) gave 85% of hydrazide **III** (Scheme 2).

Scheme 2.



5-Phenyl-1,3,4-oxadiazol-2(3*H*)-one (IIa). mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: 7.46 m (3H, H_{arom}), 7.83 d (2H, H_{arom}), 10.55 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 162 (100) $[M]^+$, 118 (29.5), 105 (19.2), 103 (6.1), 91 (16.4).

5-(4-Tolyl)-1,3,4-oxadiazol-2(3*H*)-one (IIb). mp 167–168°C. ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 7.46 d (2H, H_{arom}), 7.71 d (2H, H_{arom}), 10.63 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 176 (100) $[M]^+$, 132 (28.4), 119 (18.6), 117 (5.9), 105 (16.2).

5-(4-Bromophenyl)-1,3,4-oxadiazol-2(3*H*)-one (IIc). mp 244–245°C. ^{1}H NMR spectrum, δ, ppm: 7.65 d (2H, H_{arom}), 7.79 d (2H, H_{arom}), 10.58 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 241 (100) $[M]^+$, 197 (30.2), 184 (19.84), 182 (6.6), 170 (17.2).

4-Bromo-*N*′-(piperidinocarbonyl)benzohydrazide (III). Yield 85%, mp 202–203°C (from EtOH).

^{1}H NMR spectrum, δ, ppm: 1.58 s (6H, $3CH_2$), 3.40 s (4H, $2CH_2$), 7.28 s (1H, NH), 7.25 d (2H, H_{arom}), 7.68 d (2H, H_{arom}), 9.09 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 326 (78.2) $[M]^+$, 212 (60.6), 182 (100).

The ^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer (500.13 MHz) from solutions in $CDCl_3$; the chemical shifts were measured relative to the residual proton signal in the solvent. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument with direct sample admission into the ion source.

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