

## NOTE

## OXIDATION OF SOME PRIMARY THIOAMIDES WITH LEAD TETRAACETATE

BOJAN D. PODOLEŠOV and VERA B. JORDANOVSKA

Faculty of Chemistry, University of Skopje, Arhimedova 5, YU-91000 Skopje, Yugoslavia

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**Abstract.** The oxidation of thiobenzamide, thionicotinamide and thioisonicotinamide with lead tetraacetate was achieved. It was established that by this oxidation corresponding 3,5-disubstituted-1,2,4-thiadiazoles were obtained.

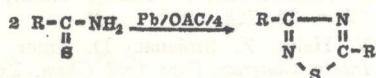
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Continuing our investigation on the oxidation of thioamides<sup>1</sup> we report on the oxidation of primary thioamides with lead tetraacetate.

For the oxidation of primary thioamides various oxidizing agents have been used: ozone<sup>2,3</sup>, iodine<sup>4,5</sup>, bromine<sup>6</sup>, N,N-dichlorocarbamate<sup>7,8</sup>, ammonium persulphate<sup>9</sup>, N-sulphonyl-*p*-toluene sulphonamide<sup>10,11</sup> and sodium nitrate<sup>12,13</sup>. In all these oxidations 3,5-disubstituted-1,2,4-thiadiazoles were obtained as main oxidation products.

To the best of our knowledge lead tetraacetate was used only in the oxidation of N-substituted thioamides and as a reaction product corresponding diimidoyl disulphide was obtained.<sup>14</sup>

In the present work, we report on the oxidation of thiobenzamide, thionicotinamide and thioisonicotinamide with lead tetraacetate. The reaction was carried out in glacial acetic acid at 60°C with constant shaking for 2 h in a 1:1 molar ratio. Under such condition all mentioned primary thioamides were oxidized to the corresponding 3,5-disubstituted-1,2,4-thiadiazoles:



R: phenyl-, 3-pyridyl-, 4-pyridyl

The obtained 3,5-disubstituted-1,2,4-thiadiazoles were identified by melting points, elemental analysis, molecular weight determination and their i.r. spectra.

In order to explain the mechanism of the reaction, further investigations are under way.

The melting points are uncorrected.

Molecular weights were determined by the vapour pressure osmometry method in benzene on a Dampdruck-Osmometer, Knauer.

**3,5-Diphenyl-1,2,4-thiadiazole.** To a suspension of 2.74 g (0.02 mol) thiobenzamide in 50 ml acetic acid 8.86 g (0.02 mol) lead tetraacetate were added. The reaction proceeds by heat release. In order to complete the reaction the mixture was stirred and kept warm at 60°. Then a few drops of ethylene glycol were added to the reaction mixture to remove any traces of unreacted lead tetraacetate. The acetic acid was evaporated under reduced pressure and the residue was washed several times with warm water to remove lead acetate. The separated precipitate was filtered off and dried. 1.3 g (54.6%) of crude 3,5-diphenyl-1,2,4-thiadiazole was obtained. The recrystallization from ethanol gave colourless needles, m.p. 88° (85—88°<sup>13</sup>). A sample mixed with authentic 3,5-diphenyl-1,2,4-thiadiazole<sup>13</sup> does not show depression of the m.p. and the i.r. spectrum of the product was identical with that of the authentic product.

Anal.: C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>S calc'd: C 70.56% H 4.23% N 11.76% S 13.45% found: C 70.36% H 4.11% N 11.88% S 13.76%

Mol. weight calc'd: 238.31, found: 232

**3,5-Di[4-pyridyl]-1,2,4-thiadiazole.** As described above by the oxidation of 2.76 g (0.02 mol) of thioisonicotinamide with 8.86 g (0.02 mol) of lead tetraacetate 1 g (41.7%) of 3,5-di(4-

-pyridyl)-1,2,4-thiadiazole was obtained. Recrystallization from ethanol gave colorless crystals m.p. 196° (194—196°)

Anal.: C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S calc'd: C 59.98% H 3.36% N 23.32% S 13.34% found: C 59.63% H 3.10% N 23.50% S 13.31%

Mol. weight calc'd: 240.28, found: 234

3,5-Di(3-pyridyl)-1,2,4-thiadiazole. Thionicotinamide (2.76 g, 0.02 mol) and 8.86 g lead

tetraacetate (0.02 mol) gave 1.1 g (45.3%) of 3,5-di(3-pyridyl)-1,2,4-thiadiazole. Recrystallization from ethanol gave colourless crystals m.p. 139° (141°).

Anal.: C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S calc'd: C 59.98% H 3.36% N 23.32% S 13.34% found: C 59.73% H 3.15% N 23.62% S 13.46%

Mol. weight calc'd: 240.28, found: 234

### ИЗВОД

## ОКСИДАЦИЈА НА НЕКОИ ПРИМАРНИ ТИОАМИДИ СО ОЛОВО ТЕТРААЦЕТАТ

БОЈАН Д. ПОДОЛЕШОВ и ВЕРА Б. ЈОРДАНОВСКА

Хемиски факултет, Универзитет во Скопје

Утврдено е дека со оксидација на тиобензамид, тионикотинамид и тиозоникотинамид со олово тетраацетат во глицерална оцетна киселина при температура од 60° се добиваат 3,5-дисулституирани-1,2,4-тиадиа-

золи. На овој начин се приготвени: 3,5-дифенил-1,2,4-тиадиазол, 3,5-ди(3-пиридил)-1,2,4-тиадиазол и 3,5-ди(4-пиридил)-1,2,4-тиадиазол.

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