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5-[4-AMINO(1,2,5)OXADIAZOLYL]-5H-[1,2,3]TRIAZOLO[4,5-*c*][1,2,5]OXADIAZOLE FROM 4,4′-DIAMINO-3,3′-AZOFURAZANE

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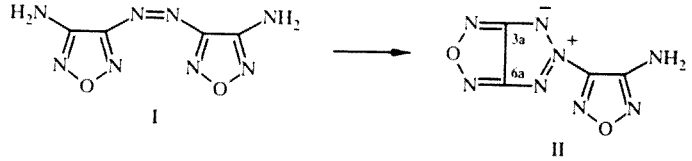
4,4′-Diamino-3,3′-azofurazane undergoes intramolecular oxidative cyclization to give 5-[4-amino(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole upon heating with $Pb(OAc)_4$ in chlorobenzene or o-dichlorobenzene or with thionyl chloride.

The formation of 1,2,3-triazole rings occurs in aromatic compounds containing amino and azo groups in the *ortho* position upon the action of certain oxidizing agents such as $Pb(OAc)_4$, $CuSO_4$, or $SOCl_2$ [1-4]. A similar transformation is also observed for 3-amino-4-phenylazofurazane [5].

We studied the action of these reagents on 4,4′-diamino-3,3′-azofurazane (I) and showed that under some of the conditions studied, I undergoes intramolecular oxidative cyclization involving the diazene fragment and one of the amino groups, leading to 5-[4-amino(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole (II).



I II

Thus, heating I with $Pb(OAc)_4$ in chlorobenzene or *o*-dichlorobenzene or with $SOCl_2$ gave II in 4-8% yield. Most of the starting reagent remains unchanged as indicated by thin-layer chromatography and the amount of I (60-84%) isolated after the reaction. The reaction does not proceed at all under conditions close to those described by previous workers [1-4], namely, heating I with $CuSO_4$ in pure pyridine or aqueous pyridine as well as heating I with $Pb(OAc)_4$ in acetic acid, benzene, or acetic anhydride.

The structure of II was established using the elemental analysis, IR, PMR, ^{13}C NMR, ^{14}N NMR, and mass spectral data.

Gunsasekaran and Boyer [6] have described a method for obtaining II† by the reduction of the corresponding azide, i.e., a compound already possessing a pentalene fragment, which, in turn, was obtained from the azido group and azo fragment as the result of thermolysis of 4,4′-diazido-3,3′-azofurazane.

*Deceased.

†Since the journal, in which the synthesis of II is described, is not readily available to us and no data are given for this compound in Chemical Abstracts, we consider presentation of the physicochemical indices of this compound worthwhile.

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EXPERIMENTAL

The IR spectrum was taken on a UR-20 spectrometer for KBr pellets. The PMR, ^{13}C NMR, and ^{14}N NMR spectra were taken on a Bruker AM-300 spectrometer in acetone-d_6. The chemical shifts for the ^{14}N NMR signals were measured relative to $MeNO_2$ as the external standard, while the ^1H NMR and ^{13}C NMR signals were measured relative to the solvent. The mass spectrum was taken on a Varian MAT CH-6 mass spectrometer. The melting point of II was taken on a Boetius heating table.

The elemental analysis data for I corresponded to the calculated values.

5-[4-Amino(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole (II). Method A. A mixture of 0.3 g (1.5 mmole) I, 50 ml dry chlorobenzene, and 1 g (2.2 mmoles) $Pb(OAc)_4$ was heated at 120-123°C for 12 h, evaporated in vacuum to dryness, and extracted with three 160-ml portions of CH_2Cl_2. The extract was dried over $MgSO_4$ and subjected to thin-layer chromatography on LSL-254 5/40 μ silica gel using 5:1 benzene—acetone as the eluent to give 24 mg (8%) II, R_f 0.52, mp 133-134°C (from benzene). IR spectrum: 3460 (NH), 3360 (NH), 1635, 1595, 1585, 1560, 1485, 1438, 1430, 1352, 1300, 1220, 1140, 1120, 1048, 1030, 960, 930, 880, 840, 815, 800, 782, 765, 724 cm^{-1}. PMR spectrum: 6.65 ppm (NH_2). ^{13}C NMR spectrum: 146.3 (C_3), 152.1 (C_4), 166.5 ppm (C_{3a}, C_{6a}). ^{14}N NMR spectrum: 18.4, −93.1, −342.4 ppm. Mass spectrum, *m/z* (I, %): 194 (27) [M^+], 138 (2) [M^+ −(NCNO)], 112 (60) [$N_2\Phi NH_2$], 84 (16) [ΦNH_2] (Φ = furazane ring).

Method B. A mixture of 1 g (5 mmoles) I, 50 ml dry *o*-dichlorobenzene, and 10 g (22 mmoles) $Pb(OAc)_4$ was heated at 135-140°C for 4 h. The precipitate was filtered off. The mother liquor was evaporated to dryness, extracted with 200 ml dry benzene, and evaporated to one-third volume. The precipitate was filtered off. The precipitates were combined, washed with 150 ml chloroform, and filtered to give 0.6 g (60%) I. The combined filtrates were evaporated to one-fifth volume and separated by thin-layer chromatography on Silpearl with benzene as the eluent. The fraction with R_f 0.11 gave 60 mg (6%) II.

Method C. A sample of 0.5 g (2.5 mmoles) I in 40 ml $SOCl_2$ was heated at reflux for 100 h. The reaction mixture was evaporated to dryness and then dried in vacuum in a desiccator over KOH. The residue was dissolved in 50 ml acetone. The solution was evaporated to one-third volume and filtered to give 0.32 g (64%) I. After concentration of the mother liquor, an additional 0.1 g (20%) I was isolated. The filtrate was evaporated to 5 ml and separated by thin-layer chromatography on Silpearl with benzene as the eluent to give 20 mg (4%) II with a slight amount of unidentified impurities.

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