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INSERTION OF A PHOSPHORUS ATOM INTO A 1,3-OXAZOLIDINE RING. STABLE β-PHOSPHONONITROXYL RADICAL WITH FIXED GEOMETRY

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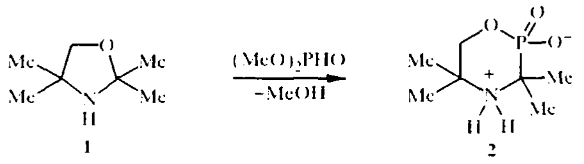
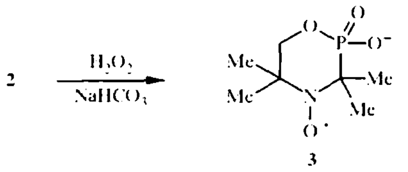
We have discovered that on interacting 2,2,4,4-tetramethyl-1,3-oxazolidine (**1**) with dimethyl phosphite insertion of the phosphorus atom into the ring occurs and an internal salt of the tetramethyl derivative of 2-hydroxy-2-oxo-1,4,2-oxaazaphosphorinane (**2**) is formed, the structure of which was confirmed by X-ray structural analysis. The reaction is accompanied by the demethylation of one of the ester functions.



Oxidation of this heterocycle in aqueous or acetonitrile solution with hydrogen peroxide in the presence of sodium bicarbonate gives the sterically hindered stable nitroxyl radical **3**, confirmed by EPR, with an endocyclic nitroxyl center and a phosphorus atom.



According to the hyperfine interaction constant this radical differs strongly from other β-phosphononitroxyl radicals of both the linear type ABP(O)CMe$_2$N(O*)Bu-*t* [1,2], and also with the nitroxyl center in a pyrroline ring but with an exocyclic β-phosphorus atom [3]. The size of a^P was small, and $a^P < a^N$ and depended weakly on the nature of the solvent (in acetonitrile a^P 4.6 Gs, a^N 16.4 Gs, in water 6.2 and 16.9 Gs respectively). The cause of the sequential reduction in solvent sensitivity of the values of a^P of β-phosphononitroxyls on insertion of

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a nitroxyl center in a ring [3], and then a phosphorus atom as well (in radical **3**) is the impoverishment of the conformational state of the radicals linked with the shutting off of the rotation around the C–N bond and further around the C–P bond on going over to the described oxaazaphosphorinane nitroxyl **3**.

3,3,5,5-Tetramethyl-2-oxido-2-oxo-1,4,2-oxaazaphosphorinane (2). A solution of oxazolidine **1** (12.9 g, 0.10 mol) and dimethyl phosphite (33.1 g, 0.30 mol) in toluene (100 ml) was heated with stirring at 110°C for 40 h. The precipitated solid was filtered off and washed with methanol. Yield 5.80 g (30%); mp 292-293°C (methanol). ^{31}P NMR spectrum (D_2O): 13 ppm. Found, %: C 43.23; H 8.33; N 6.82; P 16.07. $C_7H_{16}NO_3P$. Calculated, %: C 43.52; H 8.35; N 7.25; P 16.03.

Generation of 3,3,5,5-tetramethyl-2-oxido-2-oxo-4-oxyl-1,4,2-oxaazaphosphorinane 3. A solution of compound **2** (0.05 g), $NaHCO_3$ (0.02 g), and 32% aqueous H_2O_2 (0.14 g) in water (3 ml) or acetonitrile was stored at room temperature for 10 h, and then the EPR spectrum was recorded.

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