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PHOSPHORYLATED ISOXAZOLES

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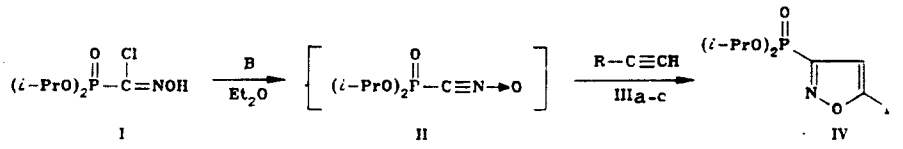
Methods are known for the preparation of phosphorylated heterocycles based on the reaction of ethynylphosphonates with diazo compounds [1, 2] in cycloaddition.

We have shown that diisopropoxyphosphorylchloroformaldoxime (I) in the presence of triethylamine or sodium bicarbonate can serve as a source of diisopropoxyphosphorylnitrile oxide (II), which facilely enters into dipolar cycloaddition with terminal acetylenes (III) at 20°C with formation of previously unknown 3-(diisopropoxyphosphoryl)-5-substituted isoxazoles (IV).



I II IV

B=$NaHCO_3$, NEt_3; IIIa, IV R=C_6H_5; IIIb R=CH_2Br, c R=$COOC_3H_7$-*i*

The process occurs regiospecifically; the yields of isoxazoles IVa-c are 69, 77, and 94%, respectively. The structure of compounds IVa-c was proven on the basis of data of PMR and ^{31}P and ^{13}C NMR spectroscopy. The PMR spectra of all the synthesized compounds in $CDCl_3$ contained a 4-H proton doublet at 6.63-7.20 ppm with spin-spin coupling constant J_{PH} = 0.9-1.5 Hz and also characteristic peaks of the corresponding protons of substituents in the 5 position of the isoxazole ring. The ^{31}P NMR spectra of compounds IVa-c contained the only peak at 2.89, 2.11, and 1.09 ppm, respectively. The data of elemental analysis for all the obtained compounds corresponded to the calculated data.

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