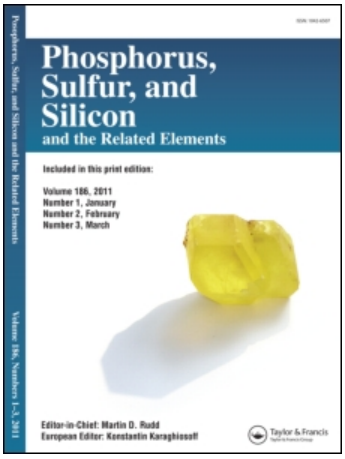

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Stereochemical Selection in Phosphoranyl Radical Formation Using Ionizing Radiation

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STEREOCHEMICAL SELECTION IN PHOSPHORANYL RADICAL FORMATION USING IONIZING RADIATION

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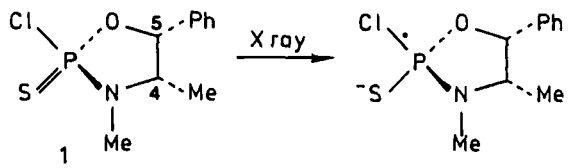
Recent electron spin resonance (ESR) experiments on phosphorus-centered radicals generated by ionizing radiation demonstrate that stereochemical aspects act strongly on the rate of radical formation and can be decisive in the selection between the possible resulting radical structures. This phenomenon was first established in a single crystal ESR study on radiogenic electron-capture phosphorus-centered radicals of the racemic and meso stereoisomers of 1,2-dimethyl-1,2-diphenyldiphosphine disulfide (1). The radiation process of the racemic form involves the formation of a symmetric species with a three-electron bond in an overall low yield. The meso isomer, on the other hand, yields exclusively asymmetric radical configurations in which the unpaired electron resides on one of the two phosphorus nuclei. The high intensity of the ESR spectra for the meso compound indicate a more efficient electron-capture process. A similar pronounced difference in radiosensitivity was observed for the R_P (1) and S_P (2) isomers of (4S,5R)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfide. Upon X irradiation, 1 readily results in an electron-capture phosphorus centered radical, whereas the concurrent process in 2 is almost completely absent. Since the geometric parameters of the atoms directly linked to phosphorus are very much alike for 1 and 2 it can be concluded that the efficiency of electron-capture at phosphorus strongly depends on the relative configuration of the distant chiral centers at C_4 and C_5.



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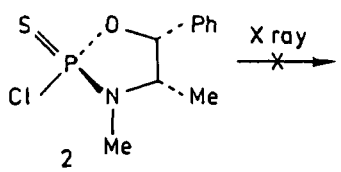

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(1) R.A.J. Janssen, M.J. van der Woerd, O.M. Aagaard, H.M. Buck, J. Am. Chem. Soc. 110, 6001 (1988).