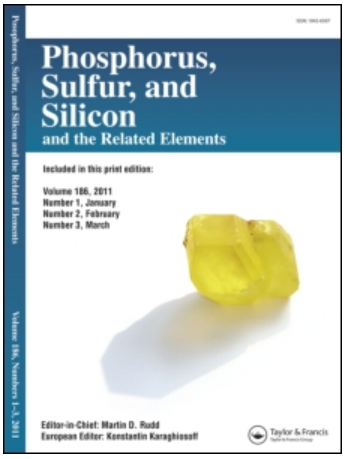

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The Structure and Reactivity of Stereochemically Rigid Phosphoranyl Radicals

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The Structure and Reactivity of Stereochemically Rigid Phosphoranyl Radicals

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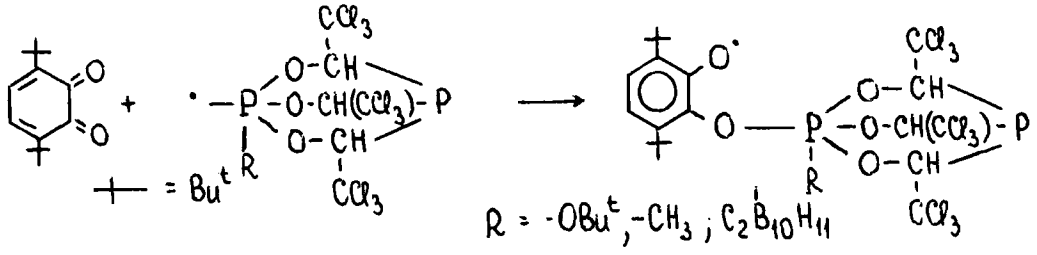
The structure and reactivity of phosphoranyls prepared by the reaction of tert.buthylperoxide with phosphorus (III) compounds, containing 5-membered cycles have been investigated. The ESR spectra of diastereomeric isomers of phosphoranils obtained from 1,2,3 oxazaphospholans displayd the difference in HFS-constants. ß-Scission rates of diastereomers was shown to differ in 1.3 time in magnititude. The reactivity of phosphoranyls formed by the interaction of tert.buthyl, methyl, boron centered carbonyl radicals with 2,6,7-tris(trichlorometyl)-1,4-diphospha-3,5,8-trioxabicyclo(2,2,2)octane was also studied. Their unusual reactivity, namely, the ability to be added to multiple C=O bonds of substituted phenoxyls occurs due to their rigid structure.



The temperature dependence of ESP spectra results from the reversible intramolecular migration of phosphoranyls between two oxygen atoms of phenoxyls. The radicals studied have got the high stereochemical rigity and stability to ß-scission.