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Synthesis, crystal structure and hydrolysis of novel isomeric cage (P-C/P-O)-phosphoranes on the basis of 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane and hexafluoroacetone

Khasiyatullina N., Mironov V., Krivolapov D., Mironova E., Gnezdilov O.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© The Royal Society of Chemistry 2016. The reaction of 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane with hexafluoroacetone leads to the simultaneous formation of regioisomeric cage (P-C/P-O)-phosphoranes, the structures of which are unequivocally confirmed by XRD. The rearrangement of the P-C-isomer to P-O-isomer with high stereoselectivity (>96%) takes place in methylene chloride solution with the retention of the phosphorus coordination. It was found that the stepwise hydrolysis of the P-O-isomer initially gives 2-(2,3-dihydroxy-1,2-diphenyl-3-trifluoromethyl-4,4,4-trifluorobutyloxy)-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphospholane as the only stereoisomer whose structure is also confirmed by XRD. Further hydrolysis of this compound leads to the formation of 2,3-dihydroxy-3-trifluoromethyl-4,4,4-trifluoro-1,2-diphenylbutylphosphate and pinacol, which forms the solvate in the crystal. Hydrolysis of the P-C-isomer yields 2-hydroxy-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphospholane, benzoin and hexafluoroisopropanol.

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