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New Aspects in the Chemistry of Some Cyclic Esters of Alkylphosphonates

C. Y. Yuan^a; S. S. Li^a; X. G. Liao^a; Z. Y. Cheng^a

^a Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, People's Republic of China

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NEW ASPECTS IN THE CHEMISTRY OF SOME CYCLIC ESTERS OF ALKYLPHOSPHONATES

C.Y.Yuan S.S.Li X.G.Liao and Z.Y.Cheng

Shanghai Institute of Organic Chemistry, Chinese
Academy of Sciences. 345 Lingling Lu, Shanghai
200032, People's Republic of China

Several new methods for the synthesis of 2-alkyl-2-oxo-1,3,2-dioxaphosphorinane (1) and -phosphhepane (2) were conducted based on Arbuzov rearrangement, alcoholysis of RP(O)Cl_2 with glycol using dilution method or alkylation of cyclic phosphite under PTC condition. The solvent effect on the ^{31}P NMR chemical shift and the characteristic behaviours of the ^{13}C NMR spectra of 1 was investigated. It was found that compd 1 with $\text{R}=\text{CH}_3$ existed in an equilibrium of e and a forms. The mass spectra of 1 and 2 showed that the ring opening was in competition with the cleavage of P-C bond. According to the fragmentation pathway, 1 can be classified in two categories involving ring opening and cleavage of C-C or P-C bond. For compd 2 the ring opening was a dominant process. Alkaline hydrolysis of 1 and 2 was studied in aqueous dioxane. The hydrolytic process is classified as an AE reaction. Quantitative structure-reactivity relationship was established by multiple regression analysis involving the rate constant and the structural parameters of the exocyclic substituents on phosphorus. The difference between the hydrolytic performance of cyclic alkylphosphonates and carboxylates was discussed in terms of various structural changes between ground state and transition state during the hydrolysis.