

## 1: Download PDF EPUB Chemistry And Application Of H Phosphonates - PDF and ePub Download Free

*Chemistry and Application of H-Phosphonates is an excellent source for those planning the synthesis of new phosphorus-containing compounds and in particular derivatives containing a phosphonate, phosphoramidate or phosphonic acid diester group.*

Chemistry and Application of H-Phosphonates is an excellent source for those planning the synthesis of new phosphorus-containing compounds and in particular derivatives containing a phosphonate, phosphoramidate or phosphonic acid diester group. The rich chemistry, low cost and easy availability of diesters of H-phosphonic acid makes them an excellent choice as synthone in a number of practically important reactions. Phosphonic acid esters are intermediates in the synthesis of important classes of compounds such as alpha-aminophosphonic acids, bisphosphonates, epoxyalkylphosphonates, alpha-hydroxyalkylphosphonates, phosphoramidates, poly alkylene H-phosphonates, poly alkylene phosphate s, nucleoside H-phosphonates. The synthesis of each of these compound classes is reviewed in detail. Alpha-Aminophosphonic acids are an important class of biologically active compounds, which have received an increasing amount of attention because they are considered to be structural analogues of the corresponding Alpha-amino acids. The utilities of alpha-aminophosphonates as peptide mimics, haptens of catalytic antibodies, enzyme inhibitors, inhibitors of cancers, tumours, viruses, antibiotics and pharmacologic agents are well documented. Alpha-Hydroxyalkanephosphonates are compounds of significant biological and medicinal applications. Dialkyl epoxyalkylphosphonates are of interest because of their use as intermediates in the synthesis of bioactive substances, and as modifiers of natural and synthetic polymers. Bisphosphonates are drugs that have been widely used in different bone diseases, and have recently been used successfully against many parasites. Poly alkylene H-phosphonates and poly alkylene phosphate s are promising, biodegradable, water soluble, new polymer-carriers of drugs. Nucleoside H-phosphonates seem to be the most attractive candidates as starting materials in the chemical synthesis of DNA and RNA fragments. The 5-hydrogen phosphonateazido-2,3-dideoxythymidine is one of the most significant anti-HIV prodrug, which is currently in clinical trials. Chapters review the synthesis; physical and spectral properties  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{17}\text{O}$  NMR data ; characteristic reactions; important classes of compounds based on these esters of H-phosphonic acid; their application as physiologically active substances, flame retardants, catalysts, heat and light stabilizers, lubricants, scale inhibitors, polymer-carriers of drugs; preparation of H-phosphonate diesters and general procedures for conducting the most important reactions. Methods for preparation and physical properties of H-phosphonates 1. From phosphorus trichloride and alcohols 1. From H-phosphonic acid 1. From white phosphorus and alcohols 1. Thermal stability Chapter 2. Structure and spectral characteristics of H-phosphonates 2. Electronic structure of phosphorus atom 2. Nature of the chemical bonds in phosphoryl group 2. Molecular structure of dimethyl H-phosphonate 2. Tautomerization of dialkyl H-phosphonates 2. Spectral characteristics Chapter 3. Reactivity of H-phosphonates 3. Acidity of H-phosphonate diesters 3. Substitution reactions at the phosphorus atom Chapter 4. Important classes of compounds 4. Poly alkylene H-phosphonates 4. Metal salts of dialkyl H-phosphonates 4. Complexes of dialkyl H-phosphonates Chapter 5. Application of H-phosphonates and their derivatives 5. Degrading and alkylating agents of polymers 5. Heat, light and UV stabilizers 5.

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How to Cite Abstract The Abramov reaction, a base-catalyzed nucleophilic addition of dialkyl H-phosphonates phosphites to carbonyl compounds, was performed with oxidized quinine derivatives as the substrates. For the C9 ketones a phosphonate $\rightarrow$ phosphate rearrangement, associated with a tandem elimination of the piperidine fragment, was evidenced. The structure involves a particular arrangement of two rigid heterocyclic fragments: Such an architecture combined with the presence of nucleophilic and electrophilic centers buried in a hydrophobic environment predestinates the molecule to asymmetric applications, such as: Synthetic modifications of the basic structure, motivated by an improved stereoselectivity potential of quinine, are an issue of ongoing trials [1]. Surprisingly, phosphorus compounds chemistry, particularly that avoiding an expansion of the core carbon skeleton [2], is poorly recognized and mainly involves esterification of different phosphorus acids with the hydroxy group [3]. These phosphorus esters were consecutively applied in organo- and metal-assisted catalysis [14,] and NMR-monitored enantiodiscrimination [21]. According to our knowledge no example of formation of a direct C $\rightarrow$ P linkage between the quinine backbone and a phosphorus atom has been reported in the literature. Stimulated by this challenge we planned to envisage a nucleophilic addition of dialkyl phosphites to quinine-based carbonyl compounds and obtain 1-hydroxyalkylphosphonate derivatives Abramov reaction, phospho-aldol reaction [22,23]. The scope, stereochemistry and side-reactions of the addition are described. Results and Discussion Quinine-based carbonyl compounds were obtained by oxidation of either the secondary C9 hydroxy group to the corresponding ketone or the vinyl group to homologous aldehydes. The last-mentioned alternative demanded a protection of the OH function. A higher scale of reaction improved the yield if compared to the literature data. Quinine 1 and Ot-butylcarbamoylquinine 2 as the substrates for oxidation of the C9 hydroxy and the vinyl group, respectively. Quinine 1 and Ot-butylcarbamoylquinine 2 as the substrates for oxidation of the C9 hydroxy a Jump to Scheme 1 Vinyl group modifications Oxidation of the vinyl group of quinine can be carried out in two different manners to give homologous aldehydes. A single-step oxidation process was not selective and produced equal amounts of diastereoisomers, The two-step procedure initially involved the use of a co-oxidizer other than periodate, e. This intermediate was preparatively separated as a The diol compound was subsequently oxidized with NaIO<sub>4</sub> to the aldehyde 4 with simultaneous C $\rightarrow$ C bond breakage. According to the literature an oxidative cleavage on silica in a two-phase system led predominantly to the C3 epimer of the R configuration In our case, when the reaction time was prolonged to 2 hours, the overall yield remained at the same level while the diastereoselectivity was reduced to Oxidation of the vinyl group of 9-O-tert-butylcarbamoylquinine to homologous aldehydes. Jump to Scheme 2 The homologous aldehyde can be prepared by oxidation of the double bond in a hydroboration $\rightarrow$ oxidation sequence, however, the presence of the nitrogen atoms, particularly that of the tertiary amino group of quinuclidine, may be troubleshooting [28,29]. Borane complexes with heteroaromatic and aliphatic amines are considered inconveniently stable in protic solvents water, alcohols and dissociate only at an elevated temperature [30]. Most probably, in our case the formation of the amine $\rightarrow$ borane complex proceeded faster than the hydroboration of the vinyl group. Again, step-by-step approach and separation of the intermediate appeared more profitable. As the oxide also released the borane $\rightarrow$ quinuclidine complex at elevated temperature the free alcohol was obtained in a satisfactory yield. The obtained aldehydes 4, 6, and 8 were reacted with 1. The presence of the tertiary amino group of quinuclidine was expected to be a sufficient catalytic base for the addition reaction, and furthermore to induce a diastereoselectivity. Addition of diethyl phosphite to aldehydes obtained in oxidation of the vinyl group. To achieve complete separation of the <sup>31</sup>P NMR signals and reliable assessment of the diastereomeric composition addition of 10 equiv of acetic acid was demanded. Partially stereoselective addition was observed for the shorter homolog 4. The R-C3 epimer gave rise to somewhat more pronounced induction. The <sup>31</sup>P

NMR resonances of the predominating forms of the hydroxyphosphonate are shifted apart by approximately 1. Thus, general stereo-controlling properties of quinine predominate and do not cooperate no matchâ€”mismatch effect visible with the absolute configuration of the starting aldehyde epimers. The hydroxyphosphonates derived from the longer homologs were completely racemic at C Two diastereoisomers of the hydroxyphosphonate 10 were formed in a ratio of 1: Elevated temperature and the presence of 1. Using toluene as the solvent, instead of benzene, the reaction time was shortened to 7 hours while maintaining the same yield [35]. Epimerization, that occurred at the neighboring C8 atom, resulted in formation of two diastereomeric products: Oxidation of quinine to quinone and quinidine and addition of phosphites to the ketones yielding the rearrangement products. Oxidation of quinine to quinone and quinidine and addition of phosphites to the ketones yieldin The reaction mixture was purified by column chromatography. Formation of four diastereomeric compounds, derivatives of epiquinidine 8R,9R , quinidine 8R,9S , quinine 8S,9R and epiquinine 8S,9S , was expected under non or partially stereoselective conditions. However, spectroscopic characterization revealed the presence of only two species one present in an overwhelming excess which exhibited the <sup>31</sup>P NMR chemical shifts not expected for phosphonates but typical for phosphates, 13b: Apparently, they were products of the phosphonateâ€”phosphate rearrangement of intermediate hydroxyphosphonates []. Treatment of ketones 11 and 12 with dimethyl- and diphenyl phosphite brought quite similar results. The expected product, diphenyl hydroxyphosphonate was not obtained, instead the quinotoxin enol diphenyl phosphate 13c appeared, and it was separated chromatographically whereas methyl monodealkylated derivative 13a precipitated directly from the reaction mixture. The selective hydrolysis of the phosphorus esters is not surprising as triethylamine and quinuclidine are bases strong enough to release the methyl ester. The additional structural modifications of the quinine skeleton of 13a were indicated with the <sup>1</sup>H,<sup>13</sup>C-HMBC correlation spectra. In addition, the characteristic signal of the H11 proton was absent and the H12 resonance was shifted to the lower field 5. The C8 resonance signal was consequently shifted from 60 ppm to approximately ppm. The aromatic system remained intact. Configuration of the predominating form can be assigned as Z. This proximity is achievable only in the case of location of vinyl and quinoline protons at the same side of the double bond. Theoretical prediction of the H12 NMR chemical shift provided an additional confirmation [39]. The chemical shift calculation performed for the opposite configuration remains in worse agreement 5. Spectroscopic features that confirmed the structure of the phosphate ester product of rearrangement and intramolecular elimination. Spectroscopic features that confirmed the structure of the phosphate ester product of rearrangement Tentative mechanism of the phosphonateâ€”phosphate rearrangement associated with tandem quinuclidine degradation. Tentative mechanism of the phosphonateâ€”phosphate rearrangement associated with tandem quinuclidine The enol phosphates 13 were not stable and underwent slow decomposition to give four to five signals in the <sup>31</sup>P NMR spectra after a month. This is a novel contribution to the reactivity of quinine although similar eliminations of piperidine in Cinchona alkaloids have been reported in the literature. The corresponding compounds were also suggested as the products of a base-catalyzed Hofmann elimination of quaternary quinuclidinium salts studied as chiral catalysts [44,45]. These unwanted rearrangement negatively influenced the stereoselective properties of the alkaloids [44,45]. An elimination associated with the phosphonateâ€”phosphate rearrangement was also reported for other 1-hydroxyphosphonate systems []. Conclusion An intriguing chemical behavior of C-9 quinine-derived ketones was demonstrated in the Abramov phospho-aldol reaction. These carbonyl compounds reacted with dialkyl and diphenyl phosphites producing quinotoxin enol phosphates that resulted from a tandem phosphonateâ€”phosphate rearrangement and an intramolecular piperidine elimination. It can be hypothesized that the driving force of the structural changes is the proximity of the tertiary amine nucleophilic center. Based on this supposition, a mechanism of the rearrangement was suggested. Supporting Information Supporting Information File 1: Experimental and analytical data.

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*"This book introduces and reviews the chemistry, characteristics and application of diesters of H-phosphonic acid and is an excellent source of ideas to those already working or who plan to work.*

Product Details Table of Contents Chapter 1. Methods for preparation and physical properties of H-phosphonates 1. From phosphorus trichloride and alcohols 1. From H-phosphonic acid 1. From white phosphorus and alcohols 1. Thermal stability Chapter 2. Structure and spectral characteristics of H-phosphonates 2. Electronic structure of phosphorus atom 2. Nature of the chemical bonds in phosphoryl group 2. Molecular structure of dimethyl H-phosphonate 2. Tautomerization of dialkyl H-phosphonates 2. Spectral characteristics Chapter 3. Reactivity of H-phosphonates 3. Acidity of H-phosphonate diesters 3. Substitution reactions at the phosphorus atom Chapter 4. Important classes of compounds 4. Poly alkylene H-phosphonates 4. Metal salts of dialkyl H-phosphonates 4. Complexes of dialkyl H-phosphonates Chapter 5. Application of H-phosphonates and their derivatives 5. Degrading and alkylating agents of polymers 5. Heat, light and UV stabilizers 5. Lubricants Promotional Information A handbook covering the synthesis, chemistry, properties and application of phosphonates, phosphoramides and diesters of phosphonic acid About the Author Kolio Dimov Troev completed his undergraduate work at Higher Institute of Chemical Technology, Sofia; received his doctorate in the field of organophosphorus chemistry in from the Institute of Organic Chemistry, Bulgarian Academy of Sciences with Prof. Georgy Borissov; and was awarded the scientific degree "Doctor of Science" in from the Institute of Polymers. In , he became Professor of Chemistry at the same Institute. He has been the founding head of the laboratory "Phosphorus-containing monomers and polymers" since His research interests are the areas of organophosphorus chemistry, especially esters of H-phosphonic acid; aminophosphonates; biodegradable, biocompatible phosphorus-containing polymers; polymer conjugates; drug delivery systems. He is also the author of two other Elsevier books, Chemistry and Application of H-phosphonates and Polyphosphoesters: Chemistry and Application Review this Product Write your message below to post a review: Ask a Question About this Product More Write your question below:

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