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Reaction of α,β-unsaturated organophosphorus compounds from chloride sulfuricum

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Abstract

This report presents the results of studying the reactions of sulphuryl chloride with α, β-unsaturated organophosphorus compounds, which were adducts of phosphorus pentachloride and nucleophiles of the formula R'CH = C(R)$PCl_3^+ \cdot PCl_6^-$ (**1**), 1-alkenyl and 2-allyloxyethyenyl dichlorophosphonates, as well as *O,O*-dialkyl-2-allyloxyethenylphosphonates. It was found that the action of sulphuryl chloride on compounds of formula (**1**) leads to chlorination of the multiple bond and conversion of the trichlorophosphonium group to dichlorophosphoryl. It is shown that the structure of the reaction products depends on the nature of the substituents at the double bond. Thus, for R = H and R' = C_2H_5O, C_6H_5 hexachlorophosphates **1**, according to IR, ^{1}H NMR and ^{31}P NMR spectra are converted to 2-ethoxy (or 2-phenyl)-1,1,2-trichloroethylphosphonic acid dichlorides. In the absence of a hydrogen atom in the α-position of the adducts **1**, substituted 1,2-dichloroethyldichlorophosphonates are formed as a mixture of diastereomers. In the presence of double bonds of various types (R = H, R' = CH_2–CH=CH_2) in the adduct **1**, an allyl group is subjected to chlorination, which leads to the formation of 2-(2,3-dichloropropoxy) ethenylphosphonic acid dichloride. It is shown that the adducts of phosphorus pentachloride with tetrahydrofuran and γ-butyrolactone react differently with sulfuryl chloride. Thus, the tetrahydrofuran adduct is converted into 2,3-dichlorotetrahydrofur-3-ylphosphonic acid dichloride, which is formed as a mixture of diastereomers. It was also obtained by the chlorination of 2,3-dihydrofur-4-yl-dichlorophosphonate with sulfuryl chloride. In the case of γ-butyrolactone, the ring is opened, which leads to the formation of 2,4-dichloro-2-dichlorophosphorylbutanoic acid chloride. To the same result results the action of sulphuryl chloride on 5-chloro-2,3-dihydrofur-4-yl-phosphonic acid dichloride. Vinyl- and 2-allyloxyethyenyl-dichlorophosphonates, unlike 1-hexenyl-, styryl- and 2-methyl-2-phenylethenyldi-chlorophosphonates, are subjected to chlorination with sulphuryl chloride. In the case of 2-allyloxyethyenyl dichlorophosphonate, allylic (1: 1) or allylic and ethenyl groups (1: 2-3) enter the reaction, depending on the mole ratio of reagents. *O,O*-Dialkyl-2-allyloxyethenylphosphonates react with sulfuryl chloride at a molar ratio of reactants of 1: 3 to give 2-(2,3-dichloropropoxy)-1,1,2-trichloroethyl-phosphonates.

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