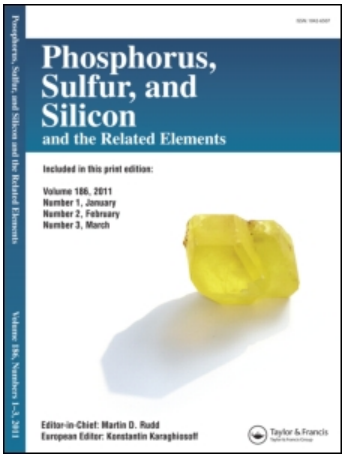

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Synthesis of Fluorinated Vinylphosphonates and Their Reactivity

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SYNTHESIS OF FLUORINATED VINYLPHOSPHONATES AND THEIR REACTIVITY

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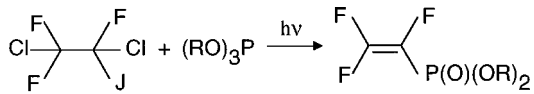
In recent years, increasing attention on the roles and significance of phosphoryl transfer has resulted in the synthesis of fluorinated phosphonates as analogues of biologically active phosphates.

Among the more interesting of these compounds, which may become key products as very convenient materials for further conversions, are trifluorovinyl-(or β-chlorodifluorovinyl)phosphonic acid derivatives. Unfortunately, these substances are difficult to prepare, although some methods of their preparation have been published.

It is well known that fluoroolefines react with various derivatives of 3-coordinated phosphorus affording fluorinated vinylphosphonates. Usually these reactions take place with higher fluoroolefines. The electrophilic nature of fluoroethylenes, especially tetrafluoroethylene, is reduced that is why trifluorovinylphosphonates stay difficult to prepare compounds.

Now we present our approach to the preparation of these substances. A single stage reaction of 1,2-dichloro-1,2,2-trifluoroiodoethane with excess (more than 2 equivalents) of trialkylphosphites leads to trifluorovinylphosphonates under UV-irradiation.



R = CH_3; C_2H_5; i-C_3H_7

SCHEME 1

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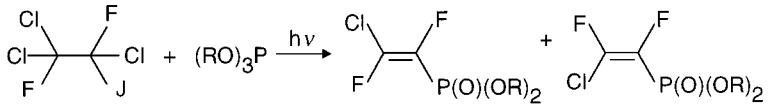
The interaction was carried out without solvents at room temperature with a good yield (~50%). Together with corresponding methylphosphonate and dialkylphosphate chloride the intermediate 1,2-dichloro-1,2,2-trifluoroethanephosphonate has been detected among of the products of the reaction. This suggests the long chain radical mechanism with elimination of two chlorine atoms from intermediate phosphonate on the last phase.

Similarly the reaction takes place with 1,1,2-trichloro-1,2-difluoroiodoethane with formation of cis and trans isomers of β-chlorodifluorovinyl phosphonic acid derivatives.



SCHEME 2

Nucleophilic substitution reactions of β-fluorine atom of trifluorovinylphosphonates on amino and alkoxy groups has been investigated:

$$CF_2 = CFP(O)(OR)_2 + R_2NSi(CH_3)_3 \rightarrow R_2NCF = CFP(O)(OR)_2 + FSi(CH_3)_3$$

Usually, these procedures lead to the mixture of cis and trans isomers.