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Free-Radical Addition of Dialkyl Phosphites to Branched Fluoro-Olefines

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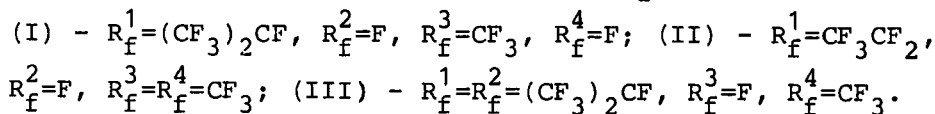
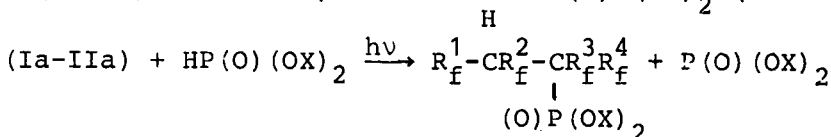
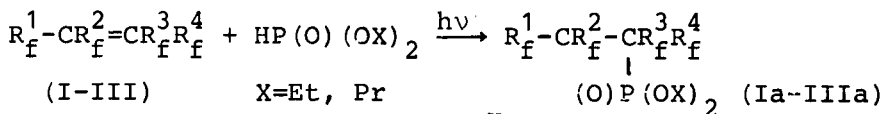
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FREE-RADICAL ADDITION OF DIALKYL PHOSPHITES TO BRANCHED FLUORO-OLEFINES

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We found that under UV-radiation, and without radical initiators, some higher fluoro-olefines regioselectively add dialkyl phosphites to give adducts with high yields. The intermediate phosphonyl substituted fluoroalkyl radicals were observed by ESR-technique and their reactivity was studied:



The capability of these radicals to abstract the hydrogen atom and therefore to conduct radical chain transformations depends on shielding of the reaction centre. Thus, in the case of perfluoro-4-methylpenten-2 the corresponding radical perishes in a few minutes under 20° without UV-radiation abstracting hydrogen atom from dialkyl phosphite. Whereas for the sterically hindered olefine - perfluoro-3-isopropyl-4-methylpenten-2 - (IIIa) the radical is stable during several weeks.

The obtained fluoroalkyl phosphonates were characterised by 1H -, ^{19}F -, ^{13}C - and ^{31}P -NMR and MS-techniques.