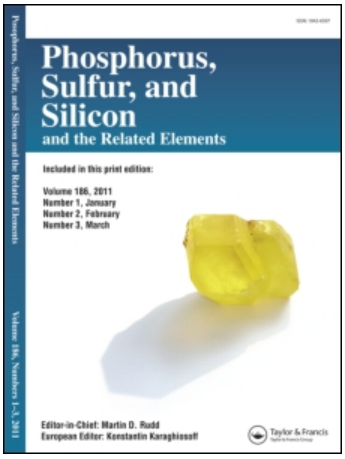

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Free-Radical Addition of Dialkyl Phosphites to Branched Fluoro-Olefines

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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:

$$R_f^1\text{-}CR_f^2{=}CR_f^3R_f^4 + HP(O)(OX)_2 \xrightarrow{h\nu} R_f^1\text{-}CR_f^2(O)P(OX)_2\text{-}CR_f^3R_f^4$$

(I-III) X=Et, Pr (Ia-IIIa)

$$(Ia\text{-}IIa) + HP(O)(OX)_2 \xrightarrow{h\nu} R_f^1\text{-}CR_f^2H\text{-}CR_f^3R_f^4 + P(O)(OX)_2$$

(I) - $R_f^1=(CF_3)_2CF$, $R_f^2=F$, $R_f^3=CF_3$, $R_f^4=F$; (II) - $R_f^1=CF_3CF_2$, $R_f^2=F$, $R_f^3=R_f^4=CF_3$; (III) - $R_f^1=R_f^2=(CF_3)_2CF$, $R_f^3=F$, $R_f^4=CF_3$.

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.