

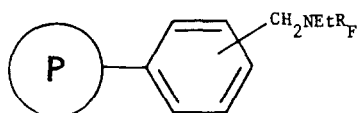
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DEVELOPMENT OF POLYMERIC ANALOGUES OF THE YAROVENKO REAGENT

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The Yarovenko reagent, $\text{Et}_2\text{NCF}_2\text{CHFC1}$, is used extensively to convert alcohols into monofluorides ($\text{ROH} + \text{Et}_2\text{NCF}_2\text{CHFC1} \longrightarrow \text{RF} + \text{Et}_2\text{NCOCHFC1} + \text{HF}$), the procedure being 'one of the simplest, most convenient, and safest fluorination techniques'. Despite this, $\text{Et}_2\text{NCF}_2\text{CHFC1}$ is not available commercially owing to its short shelf-life. We aim to circumnavigate this problem by developing an acceptable polymeric version of the reagent or of an analogous fluoroalkylamine (FAR). Work to-date on the synthesis and use of PFARS (I)-(III) will be described.



- (I) $\text{R}_F = \text{CF}_2\text{CHFC1}$
 (II) $\text{R}_F = \text{CF}_2\text{CHFCF}_3$
 (III) $\text{R}_F = \text{CF}_2\text{CF}_3$

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ADDITION OF HALOGENS TO 3-FLUORO-1-HEXYNE

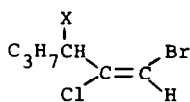
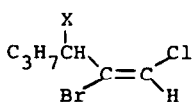
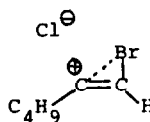
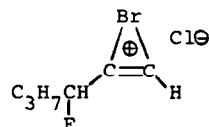
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A few years ago we reported on the addition of bromine chloride (BrCl) to 1-hexene and 1-hexyne. 1-hexyne reacts with BrCl to give Markownikoff and anti-Markownikoff products 1a and 2a in a 90:10 ratio respectively.

1a X = H1b X = F2a X = H2b X = F34

Reaction of 3-fluoro-1-hexyne with bromine and chlorine give cis- and trans-1,2-dihalo-1-hexenes. Addition of BrCl to 3-fluoro-1-hexyne gives a major product which is tentatively assigned the structure 2b. Thus reaction of BrCl with 1-hexyne and 3-fluoro-1-hexyne give intermediates 3 and 4 respectively. A possible free radical process or radical competing pathway for the reactions of halogens with 3-fluoro-1-hexyne is also considered.