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SOME ASPECTS OF THE CHEMISTRY OF POLYFLUOROALKADIENES AND POLYFLUOROALKATRIENES

Václav Dědek

Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6 (Czechoslovakia)

A convenient route for syntheses of perfluoro derivatives of 1,3-butadiene, 1,3,5-hexatriene, 1,4,7-octatriene and 1,4, 6,9-decatetraene as well as 2-chloropentafluoro-1,3-butadiene, 2,3-dichlorotetrafluoro-1,3-butadiene and 3-chlorononafluoro-1,5-hexadiene based on the photochemical addition of fluoro-halogenoethanes to fluorohalogenoethylenes is demonstrated. The reactions of dienes and trienes with alkoxides or diethylamine were studied and the stereochemistry of the products discussed. It was confirmed that the prepared compounds of 1,4-disubstituted tetrafluoro-1,3-butadiene type have a non planar cisoid structure.

The reactions of 3-chlorononafluoro-1,5-hexadiene with a series of nucleophiles (C1-, Br-, T-, F-, CN-, R0-, Et₂NH, Et₃N) show a different reactivity of both reactive centers. The perfluoroallyl chloride system in diene is of higher reactivity then the trifluorovinyl group and its reaction with a nucleophile proceeds via S_N^2 mechanism with an allylic rearrangement giving trans-isomer only. On the contrary, the trifluorovinyl group reacts obviously through a carbanion intermediate giving a mixture of cis- and trans-isomer as shown in reaction with an excess of alkoxide or diethylamine.