ADDITION OF SOME HALOALKANES TO CHLOROTRIFLUOROETHYLENE

V. Dědek and Z. Chvátal

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

It was found that the addition of some haloalkanes i.e. tetrachloromethane(I), bromotrichloromethane(II), 1,2-dibromol-chlorotrifluoroethane(III) and l-bromo-l-chloro-2,2,2-trifluoroethane(IV) to chlorotrifluoroethylene(V) in conditions of a relatively strong initiation by UV irradiation and a low concentration of olefin V gives three types of adducts resp. telomers. The reactions can be summarized as follows:

	$X = \left(\begin{array}{c} 2 \\ 2 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) \xrightarrow{X} = \left(\begin{array}{c} 2 \\ 3 \\ \end{array} \right) X$
I - IV V	
I, R ≈ CCl ₃ , X ⇒ Cl	$ R = \left[C_2 C_1 F_3 \right]_n X$
II, $R = CCl_3$, $X = Br$	
III, $R = CBrF_2CC1F$, $X = Br$	n . 0,1,2,3
IV, R = Lr _g unul, A = Dr	

.

It is shown by means of chemical transformations. ¹⁹F-NMR with shift reagent Yb(fod)₃ and mass spectrometry that the major product among 1:1 adducts in the case of addition I and II is R-CC1FCF₂-X. The products of the type $R-(C_2C1F_3)_2-X$ in the same case are mixtures of compounds in which the product of structure $R-CC1FCF_2-CC1FCF_2-X$ predominates.

The course of addition is discussed. It is assumed that the reactions are initiated by halogen atoms and the recominations of free radicals occur to a greater extent than the chain transfer.

The addition of 1,2-dibromo-1-chlorotrifluoroethylene has opened a new route for synthesis of perfluoro-1,3-butadiene, perfluoro-1,3,5-hexatriene and difluoroacetic acid.