

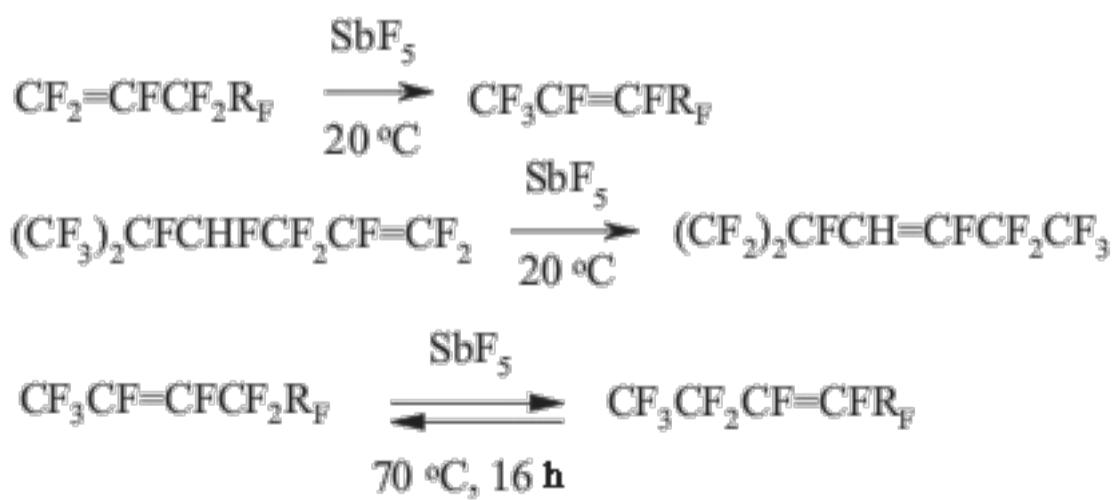
A BREAKTHROUGH IN CHEMICAL TECHNOLOGIES OF FORMING THE MULTIPLE BOND WITH FLUORINE ATOMS AND PERFLUOROALKYL SUBSTITUENTS AT IT

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7. The Migration of Double Bond in Fluoroolefines and Fluorodienes Catalyzed Antimony Pentafluoride

The isomerization of perfluoroolefines can be carried out by transforming carbocation generated for example by the SbF_5 influencing perfluoroolefine. At that terminal perfluoroolefines (perfluoropent-1-en, perfluorohex-1-en etc.) under influence of catalytic quantitites of SbF_5 are smoothly isomerized into corresponding trans-fluoroolefines with the multiple bond in the position 2 (yield is around 80-85%) [136-139]. The isomerization of perfluoro-4-methylpent-2-ene into perfluoro-4-methylpent-2-ene goes analogously to the one of perfluorobuta-1,3-dien into perfluorobut-2-en [140].



The isomerization of terminal perfluoroolefines into internal ones is carried stereoselectively and results in trans-isomers almost exclusively. Except prefluoroallylbenzene, which under the influence of catalytic quantities of SbF_5 is being isomerized into the mixture of cis- and trans-perfluoropropenylbenzenes at a rate 1:1. Pure cis- and trans-perfluoropropenylbenzenes are again forming the mixture of isomers of the same proportion under the influence of SbF_5 [141]. Other catalysts, example $AlCl_xF_y$, can be effective for that processes as well [142]. In that case, reaction period is of great importance (Table 3) [140]. Thus, the isomerization of perfluorohept-1-en at catalysis of $AlCl_xF_y$ produces the mixture of perfluorohept-2-

and perfluorohept-3-en in one hour at a ratio of 65:35.

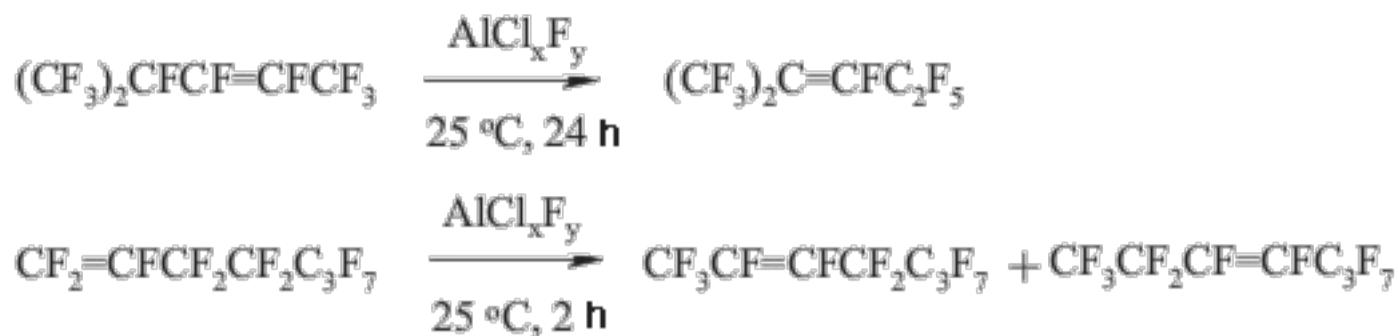
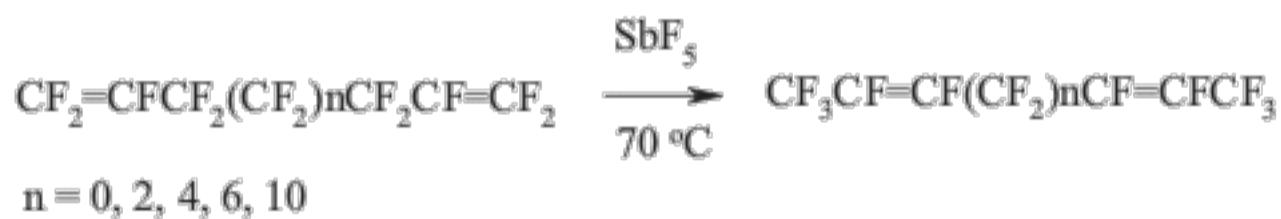


Table 3. Perfluoroheptene-1 isomerization (catalyst AlCl_xF_y) [140]

Time, h	$\text{CF}_3\text{CF}=\text{CFCF}_2\text{C}_3\text{F}_7$		$\text{CF}_3\text{CF}_2\text{CF}=\text{CFC}_3\text{F}_7$	
	trans-isomer	cis-isomer	trans-isomer	cis-isomer
1	59,3	6,4	32,0	2,3
18	15,1	1,4	78,5	4,9
66	5,2	0,9	88,8	5,2
90	5,0	0,8	89,2	5,0

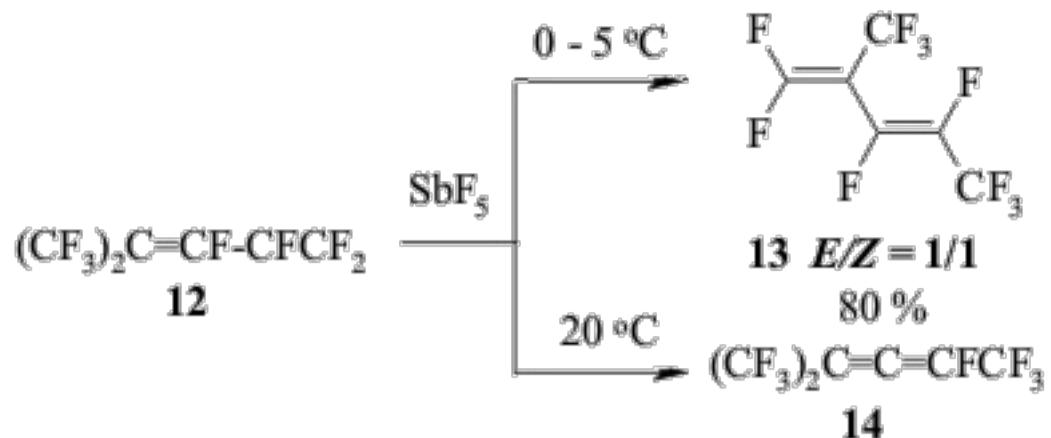
Perfluoroisopropylethylene is re-grouping into tris(trifluoromethyl)ethylene at heating up to 30-40 °C [137-139]. If a molecule has two terminal multiple bond, then they will be isomerized simultaneously, producing 80-90% E,E-isomers and 10-20% E,Z-isomers [143,144].



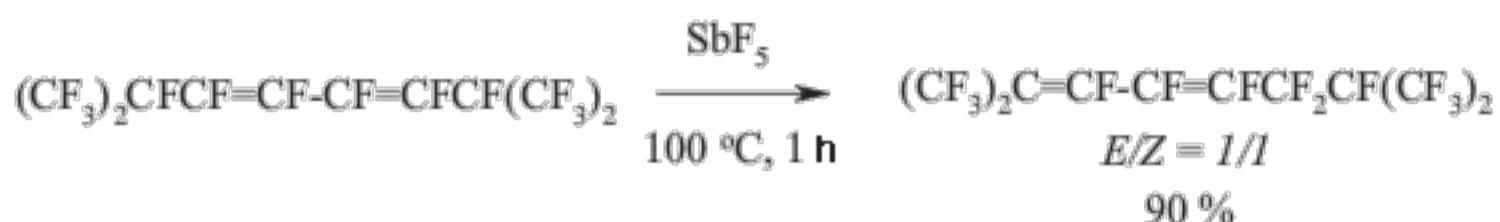
The boiling of perfluorohex-2-ene together with SbF_5 leads to the forming equilibrium mixture, containing of about 75-80 % of olefine 10 and of 20-25 % of olefine 11 [145]. All this shows us the presence of reversible 1,3-migration of fluorine in perfluoroolefines at catalysis of SbF_5 .



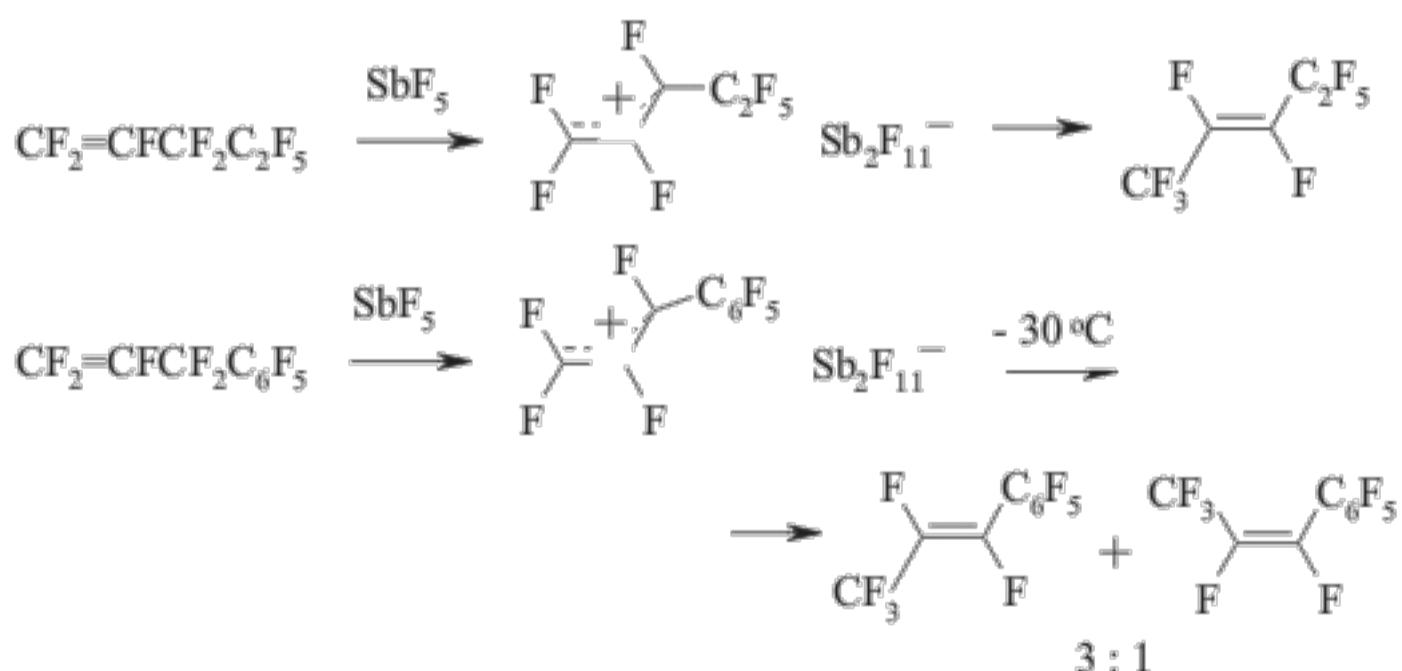
The transference of a multiple bond during the catalysis of SbF_5 can be seen among perfluorinated diens as well [146]. Thus, perfluoro(2-methylpenta-2,4-dien) 12 is being isomerized into perfluoro(2-methylpenta-1,3-dien) 13 during the influence of SbF_5 at temperature ranging from 0 to 5 °C. This compound is quantitatively transforming into tris-(trifluoromethyl)fluoroallen 14 at 20-25 °C.



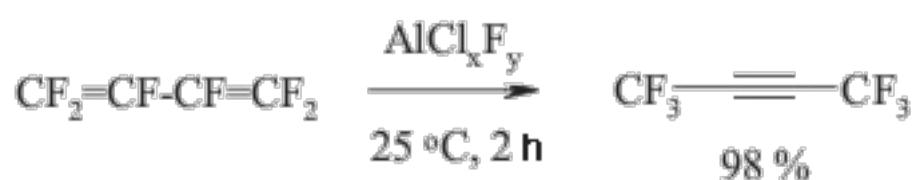
The movement of both multiple bonds along the chain is not excluded during isomerization of them both.



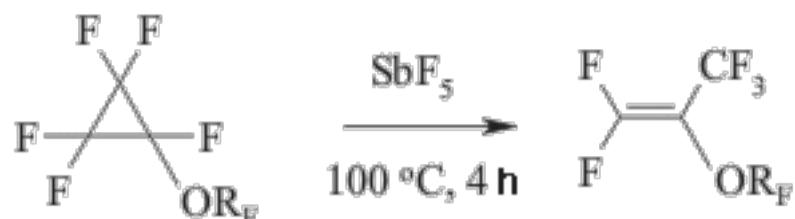
The migration of double bond under the influence of SbF_5 passes through intermediate forming of perfluoroallyl cation or via the transitional condition which is the allyl cation structure [147]. SbF_5 play a key function here . A substituent at the atom of carbon also influences the stereochemistry of the process. Thus, isomerization of perfluorobenzene results in forming of a mixture containing cis-trans-perfluoropropenylbenzenes, the decreasing of temperature of such isomerization increases the yield of trans-olefine (at -30 °C the ratio of trans/cis is 3/1) [147]. Trans isomer is a product of kinetic control.



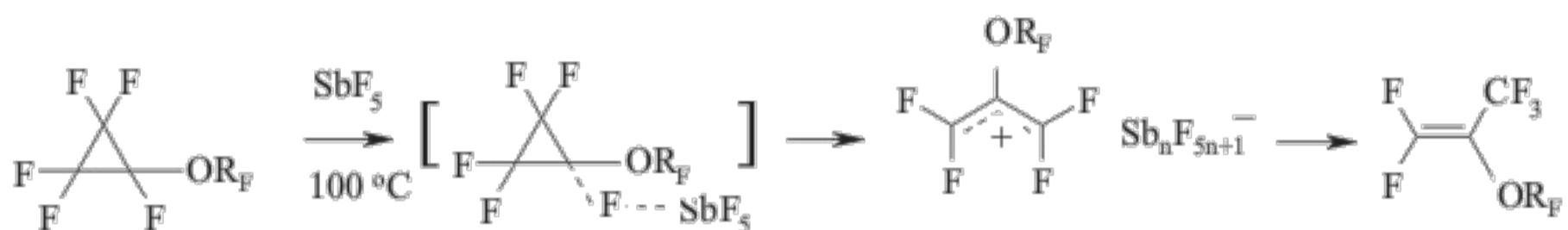
At the same time for the perfluorinated conjugate dienes the forming of a triple bond is more likely than the isomerization of multiple bonds. Actually, during the influence of AlCl_xF_y on perfluorobutadiene we obtain perfluorobut-2-ene with the quantitative yield [140].



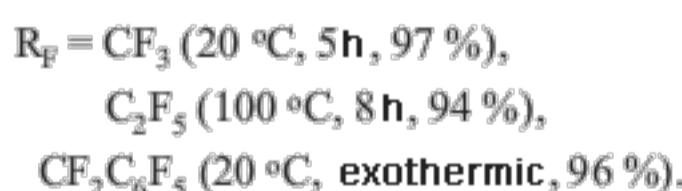
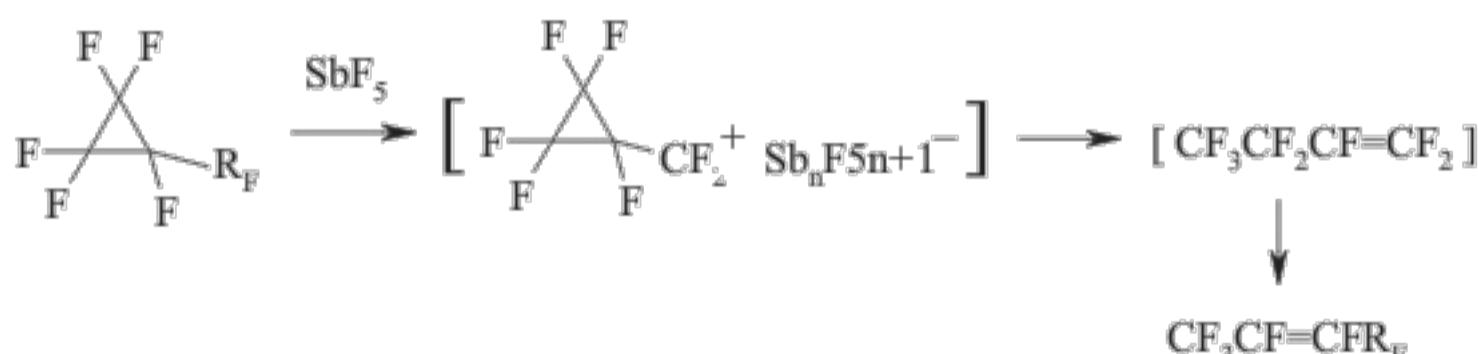
Perfluorocyclopropanes can be isomerized by SbF_5 as well. The perfluoroalkoxycyclopentanes are isomerized under the influence of SbF_5 at 100°C to perfluoro(2-alkoxipropylene) [148].



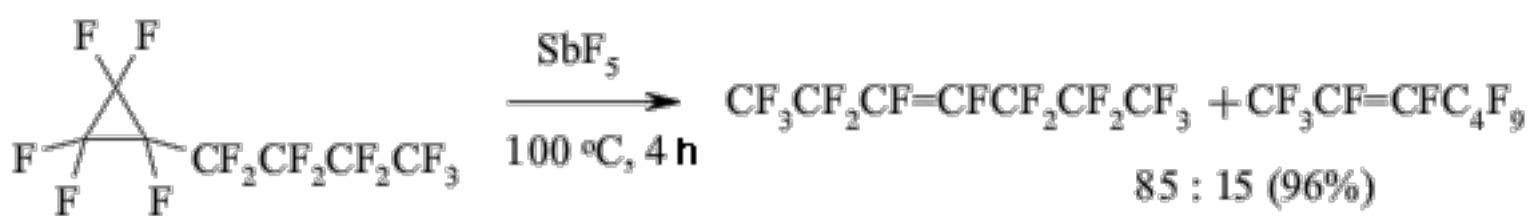
The reaction is probably carried out according to the following scheme:



The generating of carbocation is registered according to NMR ^{19}F spectra. It is rather interesting, that during the substitution of perfluoroalkoxy group for trifluoromethyl group the direction of reaction is changing significantly. For example perfluoromethylcyclopropane and perfluoro(benzylcyclopropane) are being isomerized into perfluorobut-2-ene and perfluoro(1-phenylbut-1-ene) under the influence of SbF_5 as low temperature as 20°C , while the temperature needed to transform perfluoro(ethylcyclopropane) is equal to 100°C [148].

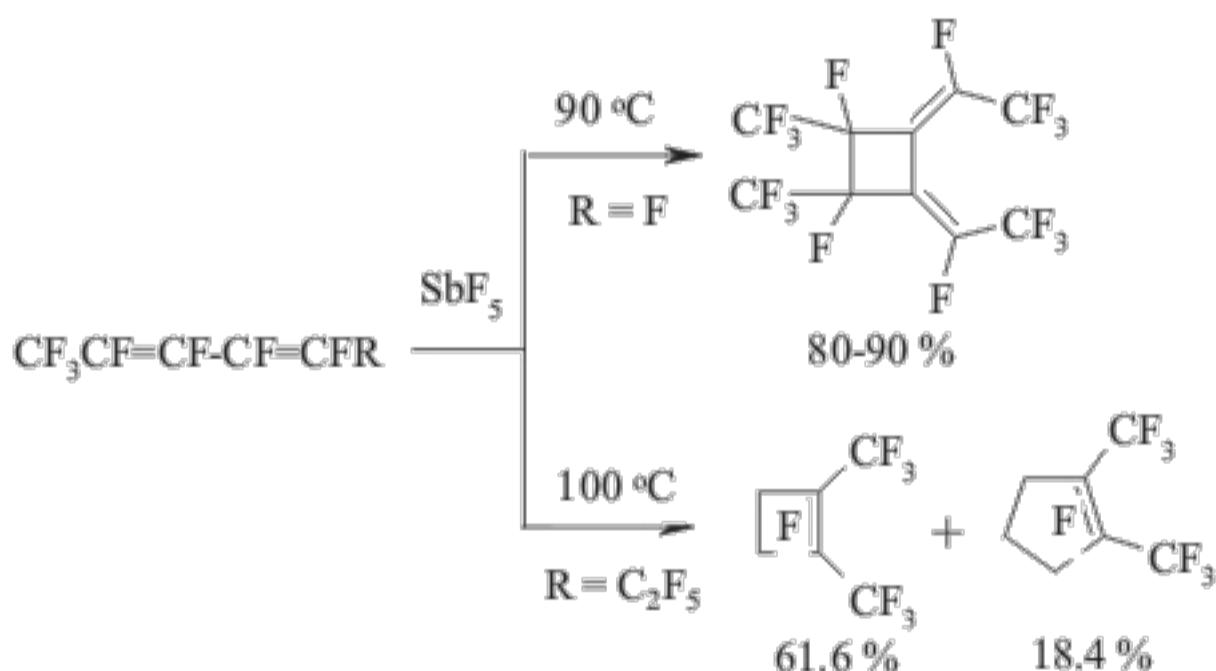
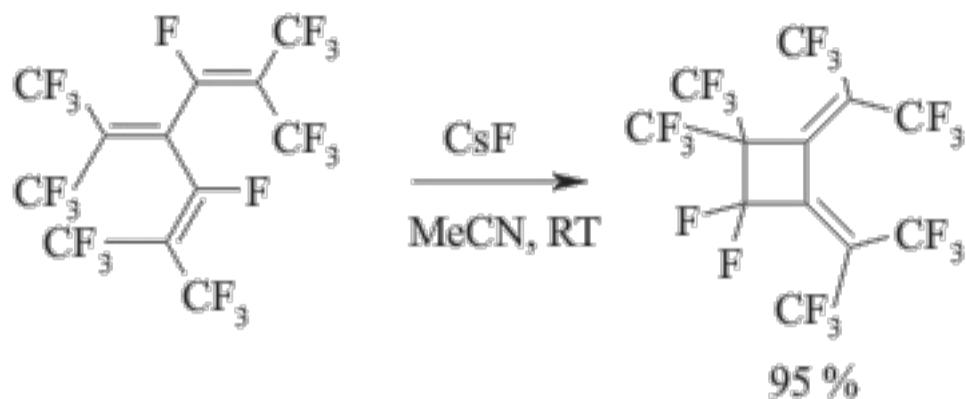


The forming of perfluorolefines mixture is possible due to the isomerization of multiple bond. Thus, perfluorobutylcyclopropane produces the mixture of perfluorobut-3-ene and perfluorohept-2-ene under the influence of SbF_5 at temperature of 100°C [148].

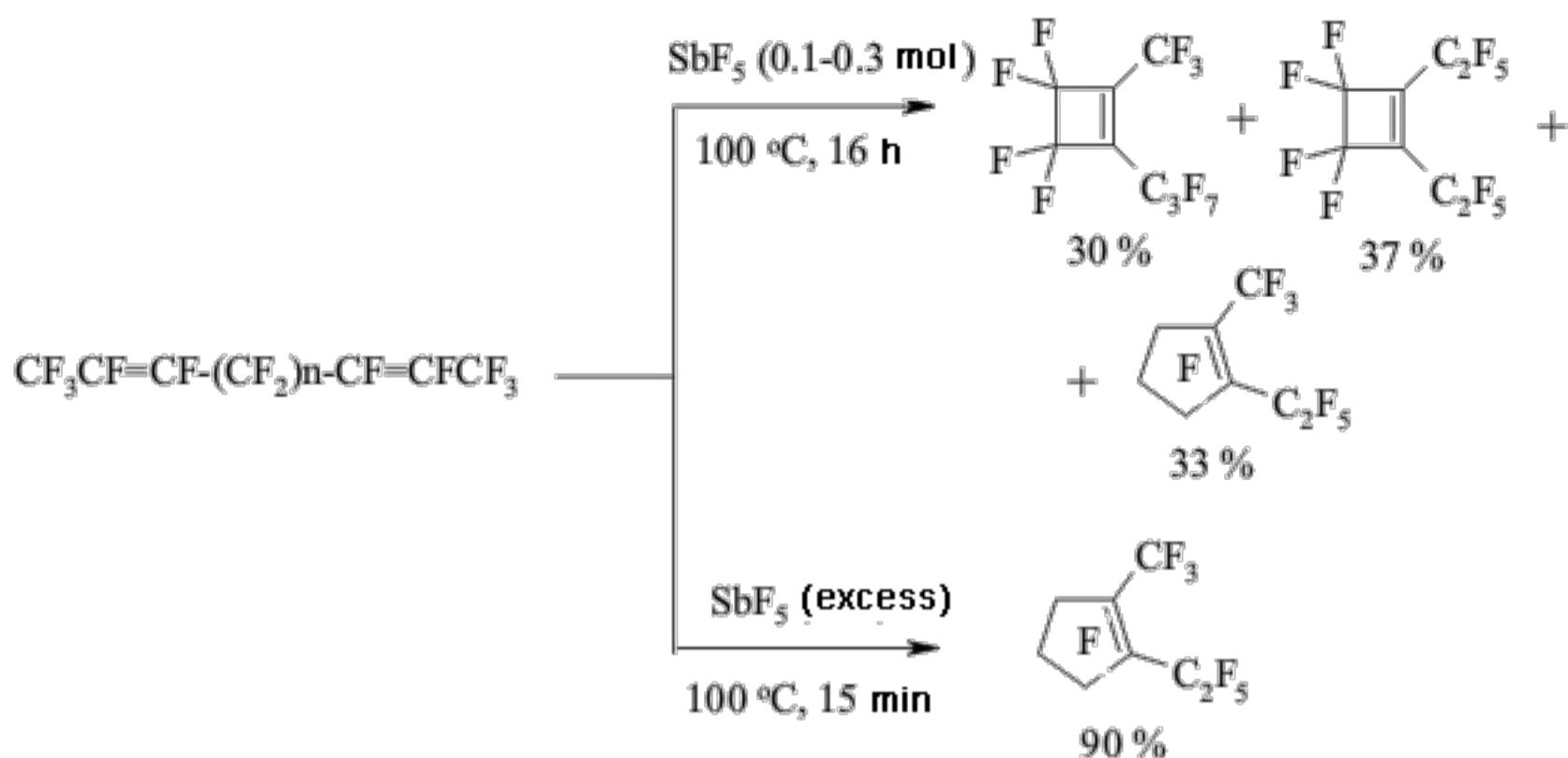


8. Synthesis of Perfluorinated Cyclic Compounds out of Fluorinated Dienes Polienes

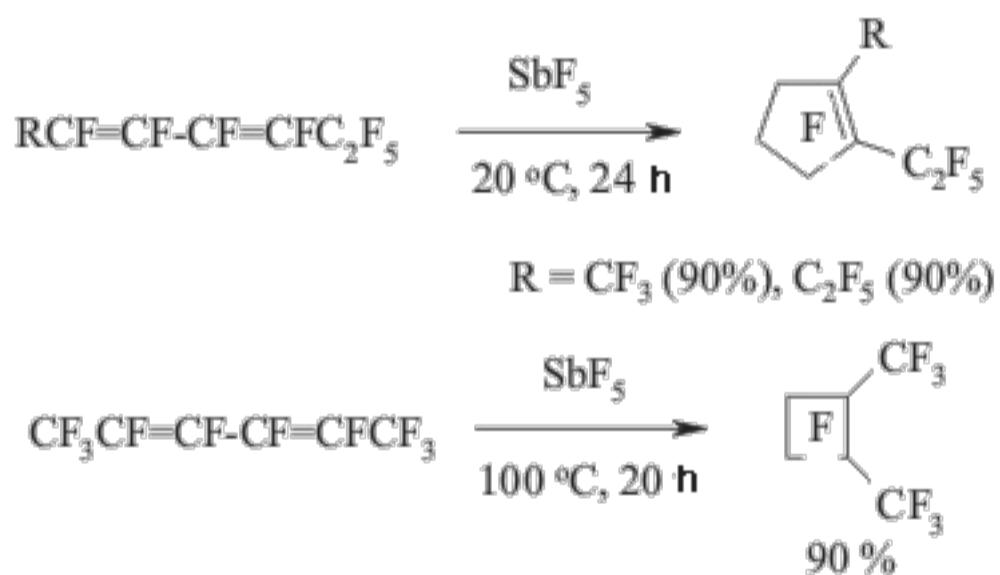
Under the influence of SbF_5 perfluorinated poliens are being subject to intramolecular cycloaddition forming tetra- or penta-member cycles [143,144].



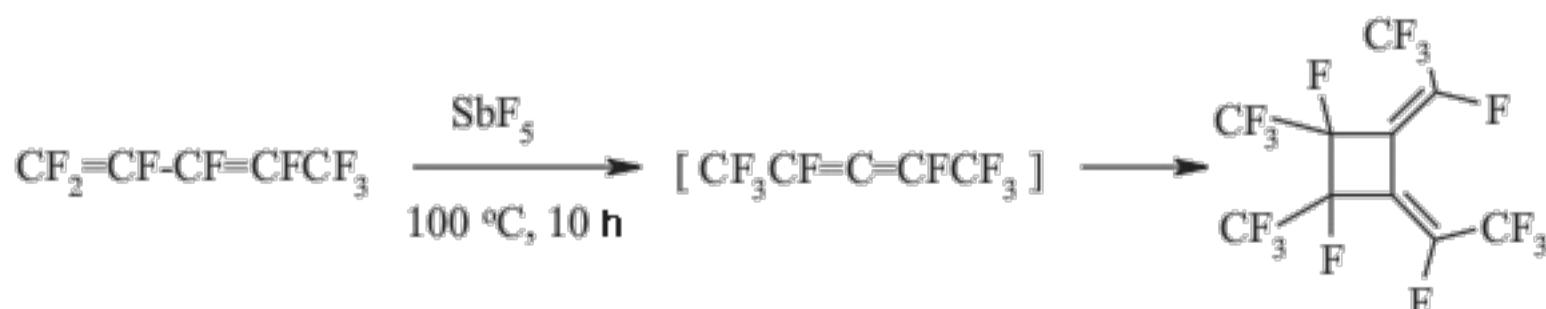
The implementing of intramolecular cyclization leading to the forming perfluorodialkylcyclopentenes is an important moment of perfluorinated die transformations in the medium of SbF_5 as German and his coworkers pro [142,146,149-151]. At that the quantities of SbF_5 are very important.



Conjugate perfluorinated dienes over SbF_5 also transform into the derivatives cyclopentene under the mild conditions. However, if a conjugate diene contains only groups, that at room temperature the cyclic product will not be formed, whereas increasing the temperature up to 100 °C perfluoro-1,2-dimethylcyclobutene is formed [146].



At the same time the presence of only one terminal CF_3 group results in forming of cyclobut system [146]. The isomerization of perfluoropenta-1,3-dien to perfluoro-1,3-dimethylallen which further cyclodimerized, may take place in SbF_5 .



Conclusion

The material listed above allows establishing the on growing researchers' interest for problem of updating the tetrafluorethylene production method and for the working out

approaches of its transforming into hexafluoropropylene and other perfluororganic compounds. The significant results achieved here prove, that they in a number of cases can become alternative for the well-known methods. We should mention a wide application of ion-fluoride as catalyst for the isomerization processes, which uncovers a possibility for synthesis of perfluoroolefines of different structure. Such processes have got obvious advantages and opportunities for the application in industrial technologies. At implementing of that methodology discovery of new reactions and transformations resulting in synthesis of fluorine containing compounds should be expected. There is no doubt that issues regarding the implementing of approaches and ideas are of interest of not only chemists working in the field of fluoroorganic compounds chemistry but of specialists in the field of organic synthesis. At that it is obvious, in a number of cases perfluoroorganic compounds are convenient and sometimes unique models for setting and solving some fundamental issues of theoretical organic chemistry.

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