Journal contents

# 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 By Antimomy Pentafluoride

The izomerization of perfluoroolefines can be carried out by transforming of carbocation generated for example by the $SbF_5$ influencing perfluoroolefine. At that the terminal pefluoroolefines (perfluoropent-1-en, perfluorohex-1-en etc.) under the 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-2-methylpent-2-ene goes analogously to the one of perfluorobuta-1,3-dien into perfluorobut-2-en [140].

$$CF_2{=}CFCF_2R_F \xrightarrow[20\,^{\circ}C]{SbF_5} CF_3CF{=}CFR_F$$

$$(CF_3)_2CFCHFCF_2CF{=}CF_2 \xrightarrow[20\,^{\circ}C]{SbF_5} (CF_2)_2CFCH{=}CFCF_2CF_3$$

$$CF_3CF{=}CFCF_2R_F \underset{70\,^{\circ}C,\ 16\ h}{\overset{SbF_5}{\rightleftarrows}} CF_3CF_2CF{=}CFR_F$$

The isomerization of terminal perfluorolefines into internal ones is carried out stereoselectively and results in trans-isomers almost exclusively. Except for 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 of 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, for example $AlCl_xF_y$, can be effective for that processes as well [142]. In that case, the reaction period is of great importance (Table 3) [140]. Thus, the isomerization of perfluorohept-1-en at catalysis of AlClxFy produces the mixture of perfluorohept-2-en and perfluorohept-3-en in one hour at a ratio of 65:35.

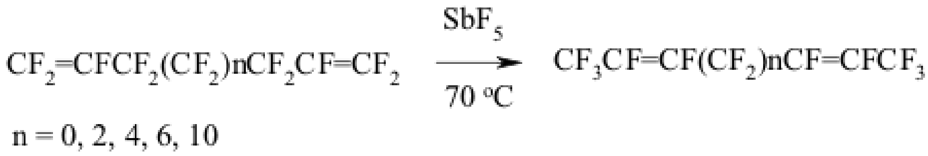
$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[25\,^{\circ}C,\ 24\ h]{AlCl_xF_y} (CF_3)_2C{=}CFC_2F_5$$

$$CF_2{=}CFCF_2CF_2C_3F_7 \xrightarrow[25\,^{\circ}C,\ 2\ h]{AlCl_xF_y} CF_3CF{=}CFCF_2C_3F_7 + CF_3CF_2CF{=}CFC_3F_7$$

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

| Time, h | $CF_3CF{=}CFCF_2C_3F_7$ | | $CF_3CF_2CF{=}CFC_3F_7$ | |
|---|---|---|---|---|
| | 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].



$$CF_2{=}CFCF_2(CF_2)nCF_2CF{=}CF_2 \xrightarrow[70\ ^{o}C]{SbF_5} CF_3CF{=}CF(CF_2)nCF{=}CFCF_3$$

n = 0, 2, 4, 6, 10

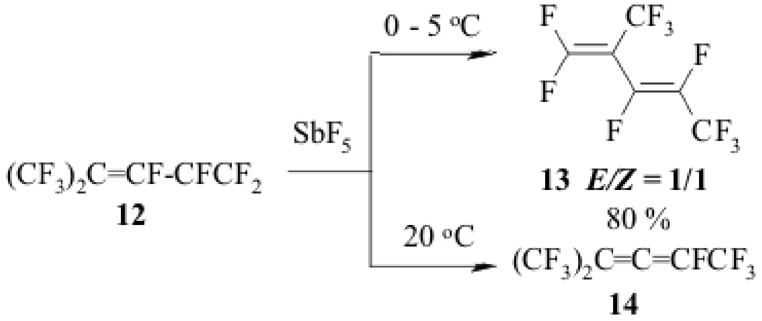
The boiling of perfluorohex-2-ene together with $SbF_5$ leads to the forming of equilibrium mixture, containing of about 75-80 % of olefine **10** and of 20-25 % of olefine **11** [145]. All this shows us the presence of reversible 1,3-migration of fluorine in fluoroolefines at catalysis of $SbF_5$.

$$CF_3CF{=}CFCF_2(CF_2)nCF_3 \overset{SbF_5}{\rightleftharpoons} CF_3CF_2CF{=}CF(CF_2)_{n-1}CF_3$$

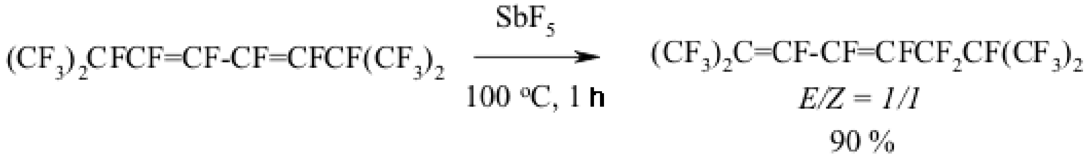
n = 1, 2

**10** **11**

The transference of a multiple bond during the catalysis of $SbF_5$ can be seen amongst 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 quantitively transforming into tris-(trifluoromethyl)fluoroallen **14** at 20-25 °C.



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

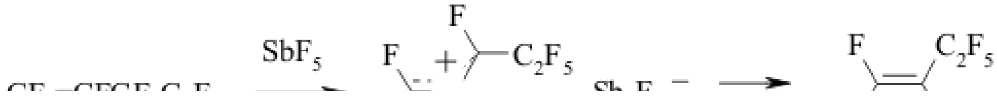


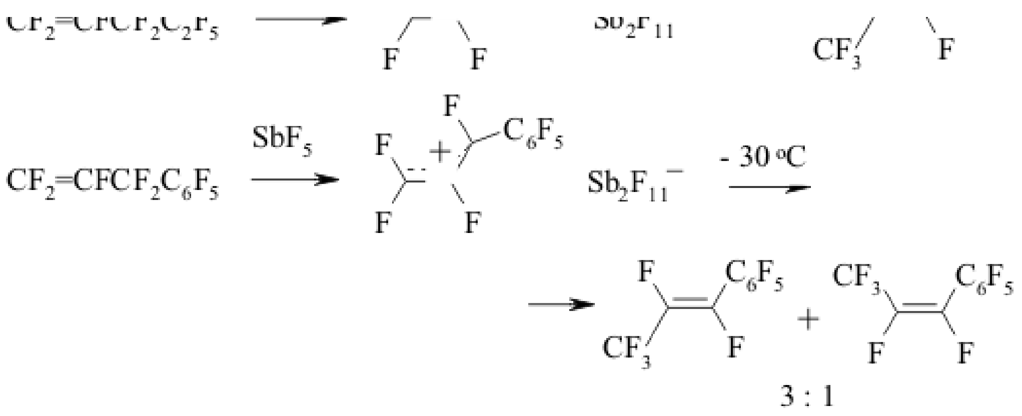
$$(CF_3)_2CFCF{=}CF\text{-}CF{=}CFCF(CF_3)_2 \xrightarrow[100\ ^{o}C,\ 1\ h]{SbF_5} (CF_3)_2C{=}CF\text{-}CF{=}CFCF_2CF(CF_3)_2$$

E/Z = 1/1

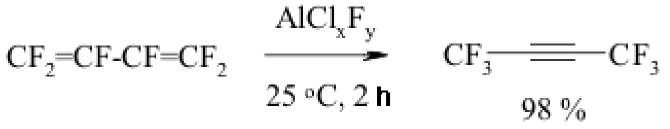
90 %

The migration of double bond under the influence of $SbF_5$ passes through the intermediate forming of perfluoroallyl cation or via the transitional condition which is like the allyl cation structure [147]. $SbF_5$ play a key function here . A substituent at the allyl atom of carbon also influences the stereochemistry of the process. Thus, the isomerization of perfluorobenzene results in forming of a mixture containing cis- and 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.



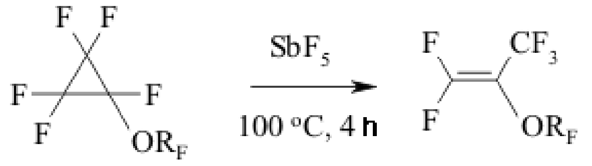


At the same time for the perfluorinated conjugate dienes the forming of a triple bond is more likely than the isomerization of multiple bonds. Actually, during the influence of AlClxFy on perfluorobutadiene we obtain perfluorobut-2-ene with the quantitive yield [140].



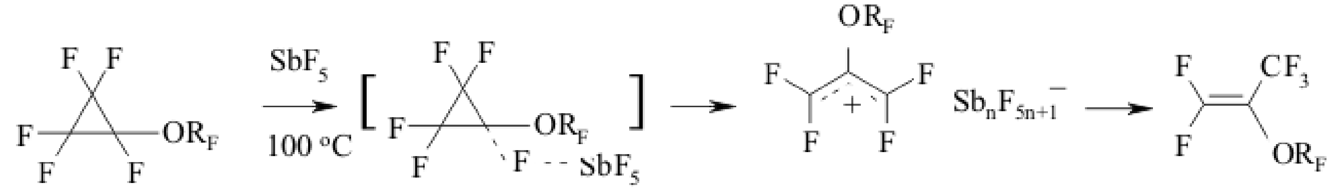
$$CF_2{=}CF\text{-}CF{=}CF_2 \xrightarrow[25\ ^{o}C,\ 2\ h]{AlCl_xF_y} \underset{98\ \%}{CF_3{-}C{\equiv}C{-}CF_3}$$

Perfluorocyclopropanes can be isomerized by $SbF_5$ as well. Thus, perfluoroalkoxicyclopetanes are isomerized under the influence of $SbF_5$ at 100 $^{O}C$ into perfluoro(2-alkoxipropylene) [148].

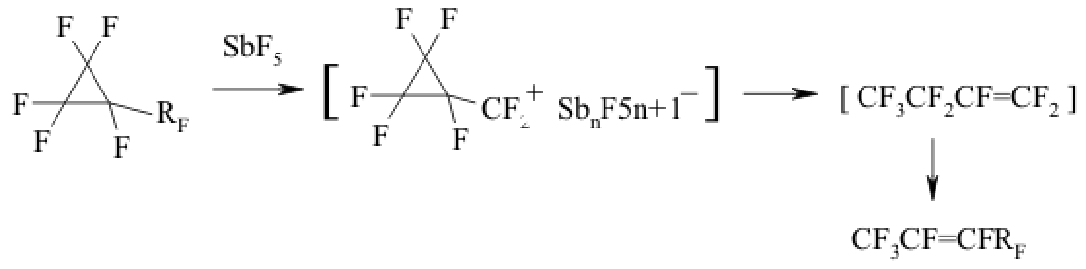


$R_F = CF_3$ (57%), $n\text{-}C_3F_7$ (64%)

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

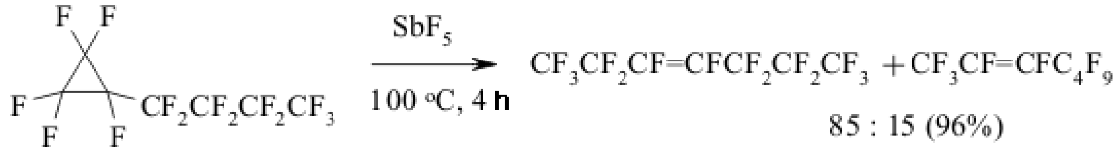


The generating of carbocation is registered according to NMR $^{19}F$ spectra. It is rather interesting, that during the substitution of perfluoroalkoxy group for trifluoromethyl group the direction of reaction is changing significantly. For example, perfluoromethylcyclopropane and perfluoro(benzylcyclopropane)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



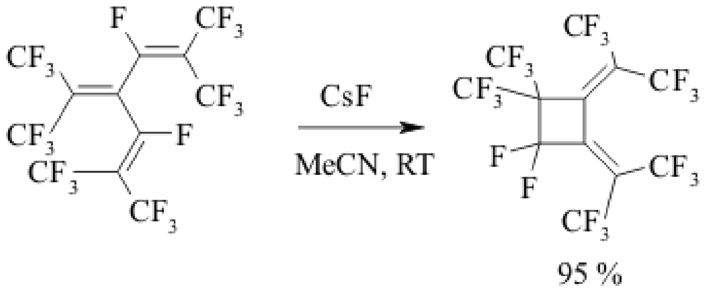
$R_F = CF_3$ (20 °C, 5h, 97 %),
$C_2F_5$ (100 °C, 8h, 94 %),
$CF_2C_6F_5$ (20 °C, exothermic, 96 %).

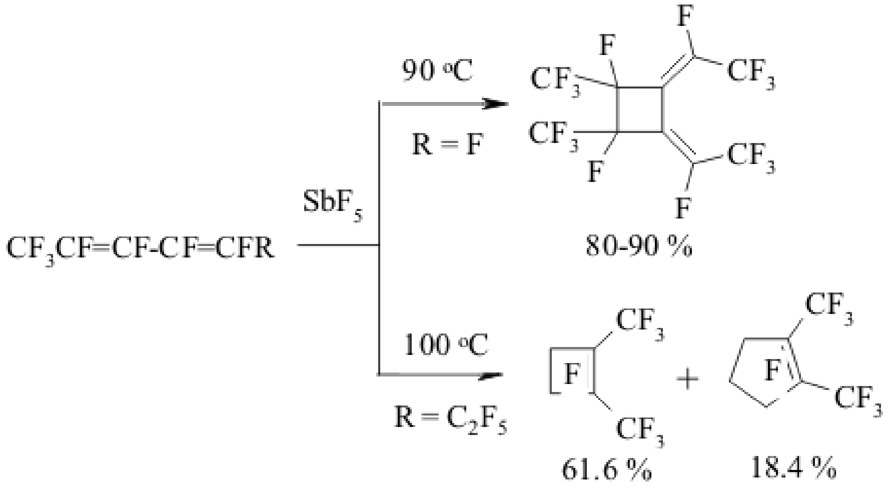
The forming of perfluorolefines mixture is possible due to the isomerization of a multiple bond. Thus, perfluorobutylcyclopropane produces the mixture of perfluorohept-3-ene and perfluorohept-2-ene under the influence SbF5of at temperature of 100 °C [148].



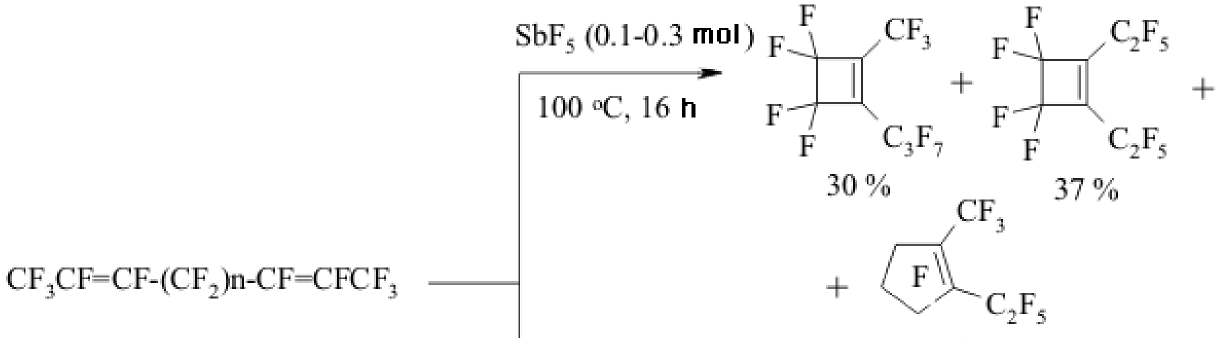
## 8. Synthesis of Perfluorinated Cyclic Compounds out of Fluorinated Dienes and Polienes

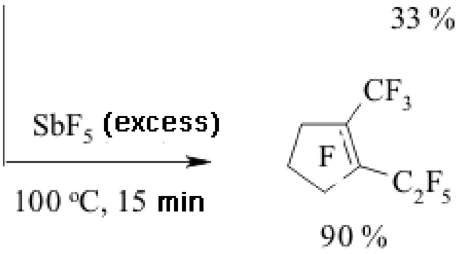
Under the influence of $SbF_5$ perfluorinated poliens are being subject to intramolecular cycloaddition forming tetra- or penta-member cycles [143,144].



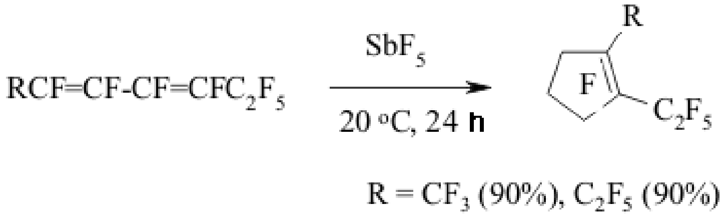


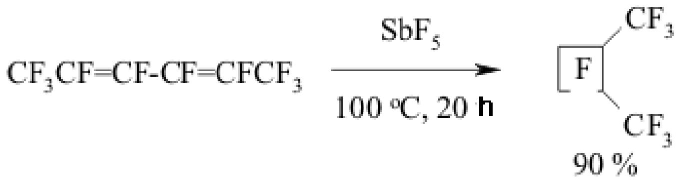
The implementing of intramolecular cyclization leading to the forming of perfluorodialkylcyclopentenes is an important moment of perfluorinated dienes transformations in the medium of $SbF_5$ as German and his coworkers proved [142,146,149-151]. At that the quantities of $SbF_5$ are very important.



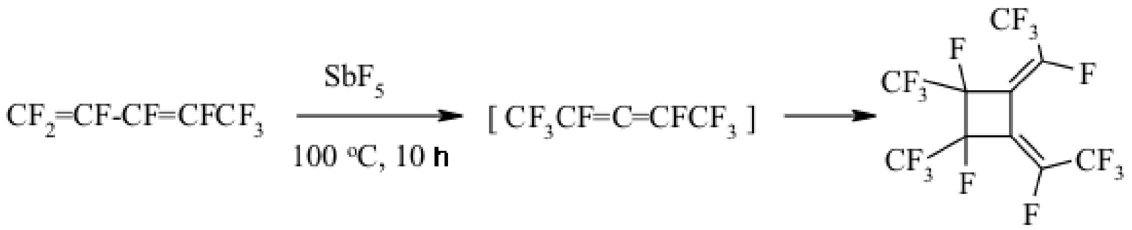


Conjugate perfluorinated dienes over $SbF_5$ also transform into the derivatives of cyclopentene under the mild conditions. However, if a conjugate diene contains only $CF_3$ groups, that at room temperature the cyclic product will not be formed, whereas by increasing the temperature up to 100 °C perfluoro-1,2-dimethylcyclobutene is formed [146].





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



## Conclusion

The material listed above allows establishing the on growing researchers' interest for the problem of updating the tetrafluorethylene production method and for the working out the 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 an alternative for the well-known methods. We should mention a wide application of ion-fluoride as a catalyst for the isomerization processes, which uncovers a possibility for synthesis of perfluoroolefines of different structure. Such processes have got obvious advantages and real opportunities for the application in industrial technologies. At implementing of that methodology a 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 new approaches and ideas are of interest of not only chemists working in the filed of fluoroorganic compounds chemistry but of specialists in the field of organic synthesis. At that it is obvious, that in a number of cases perfluoroorganic compounds are convenient and sometimes unique models for setting and solving some fundamental issues of theoretical organic chemistry.

## References

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