Journal of Fluorine Chemistry, 14 (1979) 455–466

Received: June 1, 1979

RING CONTRACTION IN THE REACTION OF POLYFLUORINATED TETRALINES WITH ANTIMONY PENTAFLUORIDE. FORMATION OF POLYFLUORINATED INDANES FROM TETRALINES

V.V.BARDIN, G.G.FURIN and G.G.YAKOBSON

Institute of Organic Chemistry, Novosibirsk, 630090, U.S.S.R.

SUMMARY

Heating of solutions of polyfluorinated tetralines containing chlorine or bromine atoms in the position 2 (2,3) in SbF_5 at 200 - 240° leads to the contraction of the alicyclic ring of tetraline to form polyfluorinated 1 - methylindanes.The six - membered alicyclic ring of perfluorotetraline and 1,1,4,4-tetrachlorooctafluorotetraline doesn't undergo any changes under the same conditions. The probable route of this reaction is discussed.

INTRODUCTION

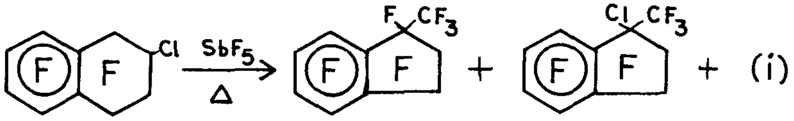
Antimony pentafluoride is one of the wide - spread catalysts for synthesis of polyfluorinated aromatic compounds [1] . The oxidative and fluorinating properties of SbF_5 extend the field of synthetic applications of this compound limiting at the same time its usage as a catalyst.

Recently the polyfluorinated benzene derivatives have been shown by us to fluorinate under the action of SbF_5 to give polyfluorocyclohexenes with substituents different from fluorine adjacent to the double bond [2] .The heating of octafluoronaphthalene with antimony pentafluoride leads to perfluorotetraline (i) [3] .2-X-Heptafluoronaphthalenes (X = H, Cl) gave under similar conditions the mixtures of tetraline (i) and undecafluorotetraline containing the substituent in the aromatic ring [4] .The fluorination of 2- bromoheptafluoronaphthalene with SbF_5 occurs dramatically to form a complex mixture in which small amounts of perfluoro - 1 -methylindan (I i) have been identified [5] .

RESULTS AND DISCUSSION

We studied the transformations of polyfluorotetralines with SbF_5 action in the course of investigation of the interaction of polyfluoroaromatic compounds with antimony pentafluoride.

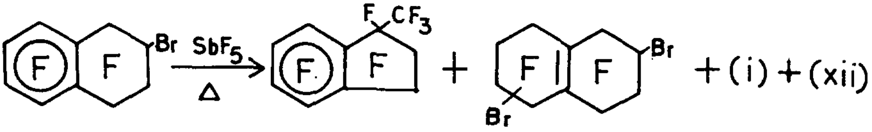
Perfluorotetraline (i),1,2,3,4 - tetrachlorooctafluorotetraline (iii) and 2 - bromoundecafluorotetraline (iv) dissolve in antimony pentafluoride at 20 - 25° without any visible changes of polyfluorinated tetralines proved by the yielding of precursors after hydrolysis of the reaction mixture.The boiling of the perfluorotetraline solution in SbF_5 with the following hydrolysis of the reaction mixture gives perfluorotetralone - 1 (v).The formation of (v) under these conditions proves the ionization of tetraline (i) goes through the elimination of a halogen atom from position 1 and generation of perfluoro - 1 - tetralinonium ion.The action of SbF_5 on 1,1,4,4 - tetrachlorooctafluoro - tetraline (vi) at 200 - 240° is accompanied by the exchange of α - chlorine atoms for fluorine to form perfluorotetraline (i).Polyfluorotetralines containing chlorine atoms in position 2 show different behaviour when heated with SbF_5. 2,3 - Dichlorodecafluorotetraline (vii) is fluorinated with SbF_5 at 200 - 240° with the ring contraction to yield 1 - chloroundecafluoro - 1 - methylindan (viii) and perfluoro - 1 - methylindan (ii).The reaction mixture contains also detectable amounts of 2 - chloroundecafluorotetraline (ix) and some tetraline (i). 2 - Chlorotetraline (ix) under the action of SbF_5 also converts to polyfluorinated indanes (ii) and (viii) with high yield. These compounds are also contained in the products of fluorination of 1,2 - chlorodecafluorotetraline (x) and 1,2,3,4 - tetrachlorooctafluorotetraline (iii).The latter is transformed in this reaction into chlorotetraline (ix) and dichlorotetraline (vii) also.



(ix) (ii) (viii)

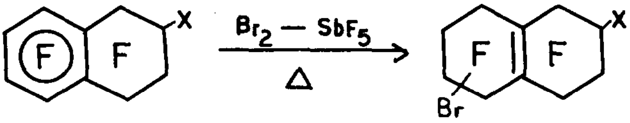
The latter data together with the results of fluorination of the tetrachlorotetraline (vi) show clearly the dependence of the route of the reaction of polyfluorotetralines with SbF_5 on the position of substituents in the alicyclic ring.

Heating of the solutions of polyfluorotetralines containing bromine atoms in the position 2 (2,3) with SbF_5 at 200 - 240° also leads to the ring contraction in these compounds but the corresponding bromoderivatives give another set of final products compared to chlorinated polyfluorotetralines. Thus, bromotetraline (iv) reacts with SbF_5 to give indan (ii), isomeric 3,8 (3,9) - dibromotetradecafluorobicyclo - [4,4, 0] - decenes - 1 (xi) and small amounts of compounds not isolated individually (xii). Nevertheless mass - spectrum and ^{19}F NMR spectral data enabled us to identify them (xii) as the products of fluorination and bromofluorination of indan (ii). Heating of 1,2 - dibromodecafluorotetraline (xiii) and 2,3 - dibromodecafluorotetraline (xiv) with SbF_5 leads to the same products with the yield of indan (ii) decreasing to 8 - 9 % and compound (xi) how the main component of the reaction mixtures.



(iv) (ii) (xi)

The formation of compounds (xi) and (xii) in the reaction of bromotetralines (iv), (xiii) and (xiv) with SbF_5 is probably connected with the oxidation of bromine under the reaction conditions. Further, the increase in the contents of halofluorination products in the case of bromofetralines compared to chlorotetralines corresponds to the lower ability of chlorine to oxidise in comparison with bromine. That is confirmed by the conversion of tetralines (i), (iv) and indan (ii) to the compounds (xv), (xi), (xii) respectively under the action of Br_2 - SbF_5 *).



X = F (i) (xv)

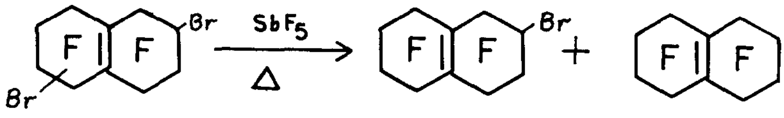
X = Br (iv) (xi)

---

* Heating of polyfluorinated tetralines with Cl_2 - SbF_5 or $SbCl_5$ - SbF_5 gives chlorofluorination products also (mass - spectral and ^{19}F NMR spectral data) but their yields were very poor compared with those of the bromofluorination reaction.

The six - membered ring contraction in naphthalene derivatives has been observed earlier in the destructive chlorination of octachloronaphthalene in the presence of $FeCl_3$ to perchloroindan [6 , 7] . The yielding of small amounts of 1 - and 2 - methylindanes from the hydrogenation products of naphthalene in the HF - TaF_5 system is the another example of such ring contraction [8] . The authors of the papers suggested the intermediate formation of corresponding tetralines but the routes from tetralines to indanes have not been discussed. The interaction of 1,1 - difluoro (dichloro) cyclohexane with SbF_5 has been shown in the paper [9] to generate 1 - fluoro (chloro)- 1 - cyclohexyl cations isomerised at the higher temperature with the ring contraction on one carbon atom. The analysis of products obtained in the reaction of polyfluorotetralines with SbF_5 leads to the suggestion that in our case the mechanism of ring contraction also involves the formation of cyclic carbocations. The generation of polyfluorinated 1 - tetralinonium ions is not accompanied evidently by the isomerisation of carbon chain as is proved by the data obtained for tetralines (i) and (vi). The participation of corresponding 2 - tetralinonium ions (or species structurally similar to this one) in the ring contraction seems to be more probable because of the rearrangement of them into indanes through the intermediate phenonium type ions. The suggestion about the route of intramolecular cyclization in polyfluorinated 2 - tetralinonium ions is based on the known fact of the formation of phenonium ions in the solvolysis of 1 - phenyl - 2 -propyltosylates and 1,2 - benzocyclenyl - 4 - tosylates [10] . A fact also indicating the participation of the aromatic ring in the alicyclic ring contraction is the result of the interaction of SbF_5 with the compound (xi), which has the same stru tural fragment 

as bromotetraline (iv) and undergoes, under the reaction conditions, fluorination with the replacement of bromine to fluorine without any alicyclic ring contraction.



(xi) (xv) (xvi)

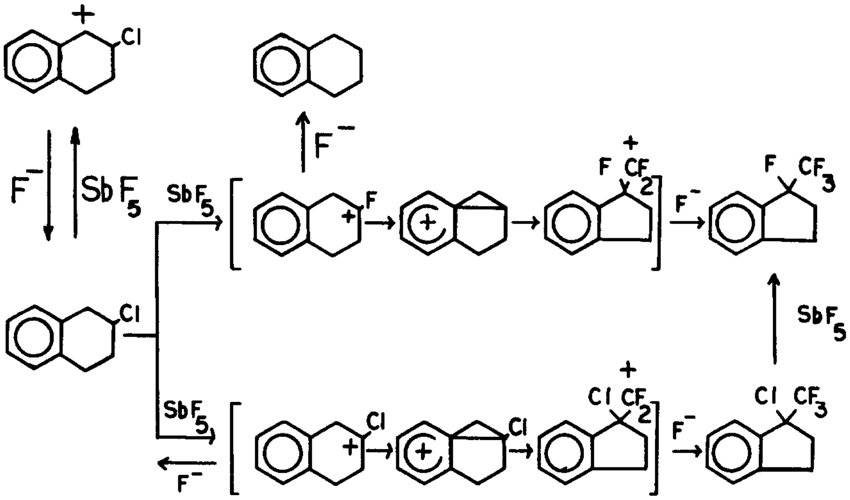
At the same time the isomerisation of 2 - tetralinonium ions by neopentyl - type rearrangements, as take place in 1 - halo - 1 -cycloalkyl cations [9], is less probable because it would lead to a mixture of polyfluorinated 1 - and 2- methylindanes, while in our case the mixtures consist only of 1 - methylindanes (ii) and (viii). By special experiments it has been shown that perfluoro - 1 - and 2 - methylindanes are stable under the reaction conditions.

The conversion of polyfluorinated tetralines into the corresponding 2 - tetralinonium ions under the action of SbF_5 can occur by soveral routes. One of them is the direct ionization of C - CL (C - Br) bond in position 2 of the fluorinated alicyclic ring that, besides ring contraction, leads to the formation of the products of replacement of chlorine (bromine) atoms by fluorine. Taking into account the formation of chloroindan (viii) from the tetralines (iii), (vii) and (ix) which cannot take place by this route it is necessary to suggest that the ionization of C - CI bond in geminal position $>CFCI$ occurs simultaneously with the loss of F^- anion which in its part leads to the formation of polyfluorinated 2 - chloro - 2 - tetralinonium ion (see [11]).

It is difficult in our case to estimate the relative contribution of polyfluorinated 2 - tetralinonium ions with cation centres $>\overset{+}{C} - F$ and $>\overset{+}{C} - CI$ in the formation of the reaction composition observed because the relative rates of their further conversions are unknown and products of these transformations can undergo considerable changes under reaction conditions, e.g. to form perfluoroindan (ii) from chloroindan (viii).

The absence of considerable amounts of 1 - bromoundeca - fluoro 1 - methylindan in the products of fluorination of bromotetralines (iv), (xiii) and (xiv) is considered to be most probably explained by its conversion into indan (ii) under the action of SbF_5. The other probable reason is the ionization of polyfluorinated bromotetralines only through the loss of Br^- ion from position 2, which is agreement with the fact of ionization of 3 - bromoheptafluorocyclohexadiene - 1,4 only by heterolysis of C - Br bond under the action of SbF_5 [5].

The discussed routes of conversion of 2-halopolyfluorotetralines into polyfluoroindanes have been shown in the scheme :



All unmarked bonds to fluorine .

The above considerations on the possible mechanism of transformation of polyfluorotetralines into indanes do not exclude the other routes of such isomerisation of carbon chain or the other description of the stages of mechanism suggested.

The initial polyfluorotetralines with substituents in the alicyclic ring were synthesized from perfluorodihydronaphthalenes-1,2 and -1,4 by the addition of chlorine (bromine) to the C = C bond or by the exchange of halogen atoms in the α-positions of polyfluorotetralines under the action of CsF or $AlCl_3$.

EXPERIMENTAL

^{19}F NMR spectra were recorded on Varian A60/56A spectrometer at 56.4 MHz (ppm from internal C_6F_6). IR spectra were recorded on Specord IR-75 instrument. Mass-spectra were recorded on MS-902 mass-spectrometer. The products were isolated by preparative scale GLC. ^{19}F NMR spectra of compounds

(vii), (ix), (xi) purified by this means are identical to the literature data [12, 13, 14] ; their molecular weights obtained from mas- spectra are correct. The compounds (iii), (vii) [13] , (iv) (xi) [14] were obtained by known methods. The characteristics of new compounds (v), (vi), (ix), (x) and (xiv) are summarized in Table 1 .

1,2 - Dichlorodecafluorotetraline, (x), (n.c.)

10.3 g perfluorodihydronaphthalene - 1,2 and 13.5 g PCI_5 were heated in a sealed tube for 14 h at 200 - 210° ,cooled, poured into water and extracted with $CHCI_3$. Organic layer was washed free from acid and dried. Evaporation of solvent yields tetraline (x) (10.1 g, 80 %) b.p. 218 - 219°.

2 - Chloroundecafluorotetraline,(ix), (n.c.)

5.2 g tetraline (x) and 4.6 g CsF were heated in a sealed tube for 14 h at 250° , cooled and steam - distilled. The product was dried to yield tetraline (ix) (3.4 g, 68 %), b.p. 187 - 190°.

2,3 - Dibromodecafluorotetraline, (xiv), (n.c.)

10.0 g perfluorodihydronaphthalene - 1,4 , 10 g bromine and 40 ml anhydrous CCI_4 were heated in sealed tube for 159 h at 200°, cooled, washed with 10 % aq. $K_2S_2O_5$ and water and then dried. Solvent was removed by distillation and the residue distilled under reduced pressure to give tetraline (xiv) (11.1 g , 75 %),m.p. 56 - 57° (from EtOH).

1,1,4,4 - Tetrachlorooctafluorotetraline, (vi), (n.c.)

5.0 g perfluorotetraline and 4.2 g anhydrous $AICI_3$ were stirred for 1 h at 60 - 70°,then 5 ml anhydrous CCI_4 was added and stirred 1 h more. The mixture was cooled, washed with HCI and water then dried, the solvent was evaporated and the residue crystallized from EtOH to yield tetraline (vi), (4.4 g, 74 %), m.p. 86 - 87°. ^{19}F NMR spectrum consisted of three signals at - 48.9 ($F_{2,2,3,3}$), - 35.6 ($F_{5,8}$), - 15.1 ($F_{6,7}$).

TABLE 1

Characteristics of the compounds (v), (vi), (ix), (x), (xiv)

Compound	Found, %			M *)	Requires, %			IR spectral data (cm^{-1}) (Fluorinated aromatic ring)
	C	Hal	F		C	Hal	F	
$C_{10}OF_{10}$ (v)	36.4		57.6	326	36.8		58.2	1747(C O), 1622, 1519, 1486
$C_{10}Cl_4F_8$ (vi)	28.7	35.8	36.8	412(^{35}Cl)	29.0	34.3	36.7	1642, 1617, 1532, 1485
$C_{10}ClF_{11}$ (ix)	32.5	10.5	57.3	364(^{35}Cl)	32.9	9.7	57.4	
$C_{10}Cl_2F_{10}$ (x)	31.1	18.6	49.5	380(^{35}Cl)	31.5	18.6	49.9	1629, 1520, 1484
$C_{10}Br_2F_{10}$ (xiv)	25.4	34.1	41.0	468(^{79}Br)	25.5	34.0	40.5	1642, 1534, 1500

* Mass - spectral data

Reaction of polyfluorotetralines with SbF_5

Polyfluorotetraline was dissolved in SbF_5 and the temperature of the bath raised to 240° , simultaneously the products obtained were distilled, then washed with water and dried. The amounts, yields and compositions of reaction mixtures are summarized in Table 2 .

Perfluorotetralone - 1, (v), (n.c.)

^{19}F NMR spectrum : - 57.9 (2 F_4), - 37.2 (2 F_2), - 30.8 (2 F_3 + F_8), - 28.3 (F_5), - 24.7 (F_6), - 18.1 (F_7).

1 - Chloroundecafluoro - 1 - methylindan, (viii), (n.c.)

^{19}F NMR spectrum : - 92.7 (CF_3), - 57.8 (2 F_3), - 51.8 (F^A_2), - 38.8 (F^B_2), - 30.3 (F_7), - 24.8 (F_6), - 19.7, - 18. ($F_{4,5}$); J^{AB}_{FF} = 251 Hz, J (F^A_2 - CF_3) = 4 Hz, J (F^B_2 - CF_3) = 18 Hz. M (mass - spectrum) 364 (^{35}Cl), $C_{10}ClF_{11}$.

Reaction of indan (viii) with SbF_5

0 .23 g indan (viii) was treated with 0.2 g SbF_5 as above, to give 0.21 g material containing 12 % (viii), and 61 % indan (ii) (GLC data).

Reaction of compound (xi) with SbF_5

11 g compound (xi) was treated with 2 g SbF_5 as above, to give 1.0 g material containing 83 % of precursor, 2 % (xv) and 1 % (xvi) (GLC data).

Reaction of compounds (i), (ii), and (iv) with Br_2 - SbF_5

The compound was dissolved in Br_2- SbF_5 and worked up as above, then washed with 10 % aq. $K_2S_2O_5$, water and dried. The amounts, yields and compositions of reaction mixtures are summarized in Table 3.

TABLE 2

Reaction of polyfluorinated tetralines with antimony pentafluoride

Tetraline, g		SbF_5, g	Yield, g	Reaction mixture, % *)		
				Tetralines	Indanes	Others
Perfluorotetraline, 3.0	(i)	17.0	2.0	i- 43,		v - 52
2- Chloroundecafluorotetraline, 2.8	(ix)	5.0	2.5	i - 4, ix - 3,	ii - 67, viii - 9	
2,3- Dichlorodecafluorotetraline, 2.3	(vii)	3.3	1.9	i - 1, ix - 10,	ii - 60, viii - 11	
1,2-Dichlorodecafluorotetraline, 3.1	(x)	4.5	2.5	i - 1, ix - 11,	ii - 49, viii - 10	
1,2,3,4- Tetrachlorooctafluorotetraline, 7.8	(iii)	13.0	6.6	i - 3, ix - 21, vii - 3,	ii - 22, viii - 20	
1,1,4,4- Tetrachlorooctafluorotetraline, 1.5	(vi)	4.7	1.0	i - 70		
2- Bromoundecafluorotetraline, 2.8	(iv)	2.8	2.8	i - 1, iv - 27,	ii - 17 ,	xi - 27, xii - 11

2,3-Dibromodecafluorotetraline, (xiv)				
4.7	5.5	3.6	i - 1, iv - 25, xiv - 11, ii - 9, xi - 19, xii - 9	
1,2-Dibromodecafluorotetraline, (xiii)				
3.9	4.7	3.0	i - 1, iv - 40, ii - 8, xi - 35, xii - 3	

* Content of each other compounds is less than 8 % (GLC data).

TABLE 3

Reaction of compounds (i), (ii), (iv) with Br_2 - SbF_5

Compound, g	SbF_5, g	Bromine, g	Yield, g	Reaction mixture, % *, +)
Perfluorotetraline, (i)				
4.5	3.6	2.0	4.6	i - 43, xv - 28
2-Bromoundecafluorotetraline, (iv),				
6.6	5.0	4.4	5.7	xi - 48, xvii - 15
Perfluoro-1-methylindan, (ii),				
0.9	2.5	0.9	0.8	xii - 77

* Content of each other compounds is less than 10 % (GLC data).

\+ 2-Bromoheptafluorotetralindione-1,4 (xvii) was isolated by preparative TLC and compound (xv) was isolated by preparative scale GLC.

2 - Bromoheptafluorotetralindione - 1,4, (xvii), (n.c.)

^{19}F NMR spectrum : - 56.7, - 34.7 (2 F_3, AB system), - 30.5 ($F_{5,8}$), - 23.9 ($F_{6,7}$), - 14.9 (F_2) ; J_{FF}^{AB} = 276 Hz , $J_{FF}^{2,3}$ = 19 Hz. M (mass- spectrum) 364 (^{79}Br), $C_{10}BrO_2F_7$.

Bromopentadecafluorobicyclo- [4,4,0]- decene- 1,(xv),(n.c.)

M (mass - spectrum) 484 (^{79}Br), $C_{10}BrF_{15}$.

REFERENCES

1 G.G.Yakobson, V.M. Vlasov,Synthesis, (1976) 652.

2 V.V. Bardin,G.G.Furin,G.G.Yakobson,Izy.Sib.Otd.Akad. Nauk S.S.S.R., Ser. Khim. Nauk, (1978) (6) 142.

3 V.V. Bardin,Yu.V.Pozdnyakovich,V.D.Steingarts,Pat.U.S.S.R. 491 605 (1974); C.A., 84 (1976) 30536 .

4 Yu.V.Pozdnyakovich,V.D.Steingarts, Zh. Org. Khim., 14 (1978) 2237.

5 Yu.V.Pozdnyakovich , V.V.Bardin,A.A.Stark,V.D.Steingarts, Zh. Org. Khim., 15 (1979) 656.

6 V.I.Shvemberger, Zh. Obshch. Khim., 8 (1938) 1353 ; C.A., 33 (1939) 4232.

7 E. Zorkendorfer, E.Boberg, J. Label. Comp., 8 (1972) 567 .

8 J. Wristeres, J. Amer. Chem. Soc., 99 (1977) 5051.

9 J. G. Olah, G. Liang, Y. Mo, J. Org. Chem., 39 (1974) 2394.

10 Ch.Lancelot, D. Cram, and P. v. R. Schleyer , Carbonium Ions, v.3, Wiley - Interscience, New - York , 1972 , p. 1347.

11 V.D.Steingarts, P.N.Dobronravov, Zh. Org. Khim., 12 (1976) 2005 ; C. A., 86(1977) 72059.

12 N.G.Malyuta,V.E.Platonov,G.G.Furin, G.G.Yakobson, Tetrahedron, 31 (1975) 1201.

13 L.S.Klimenko,V.M.Karpov,V.E.Platonov,G.G.Yakobson, Zh.Org.Khim., 15 (1979) 146.

14 T.W.Bastock,A.E.Pedler, J.C.Tatlow, J.Fluor. Chem., 8 (1976) 1