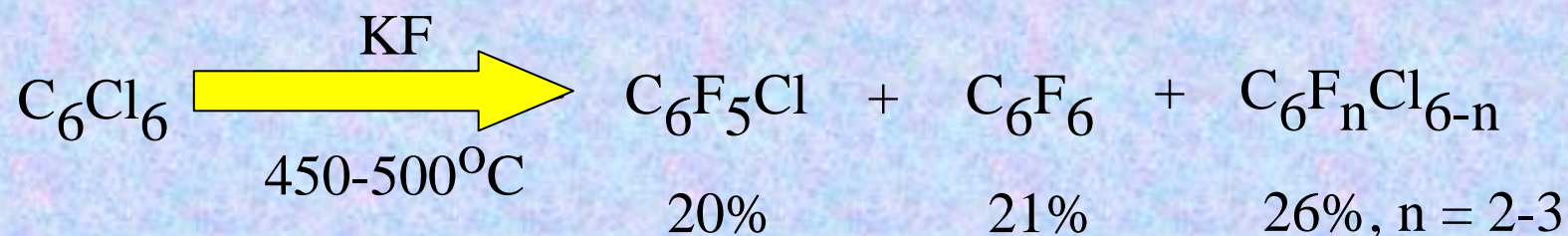


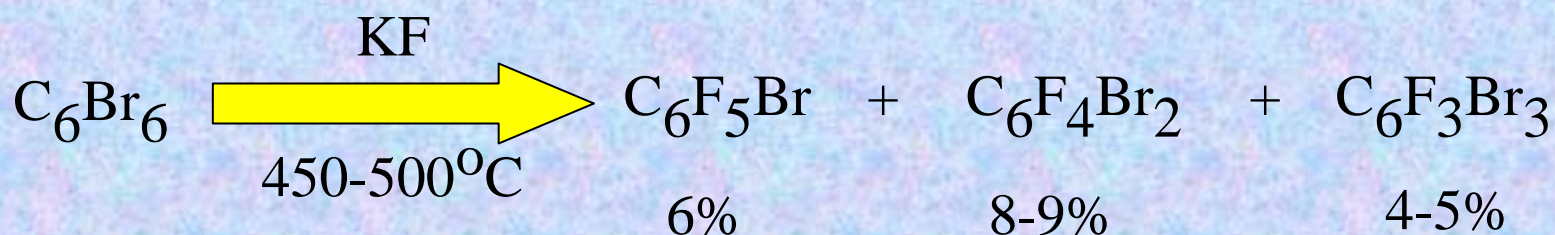
**NEW ASPECTS OF
POLYFLUOROAROMATIC CHEMISTRY:
REPLACEMENT OF –SH BY Cl AND Br;
ORGANOZINC COMPOUNDS FROM
POLYFLUOROGALOGENO- AND
PERFLUOROARENES.**

V.E. Platonov

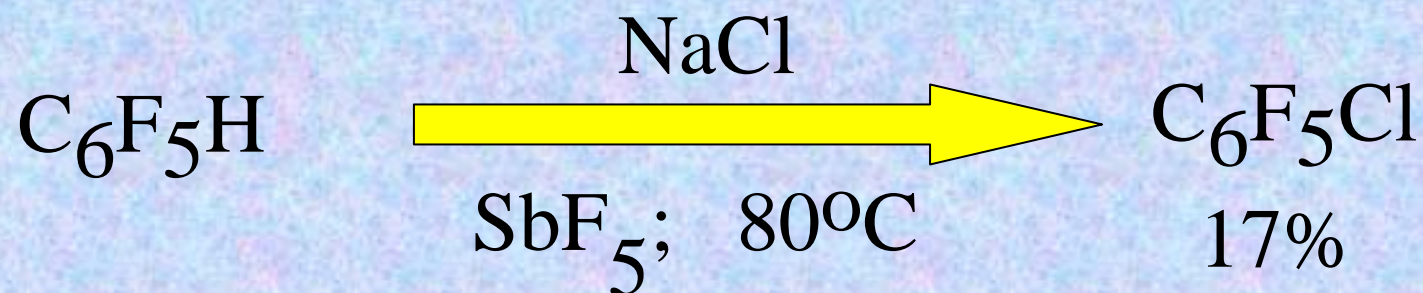
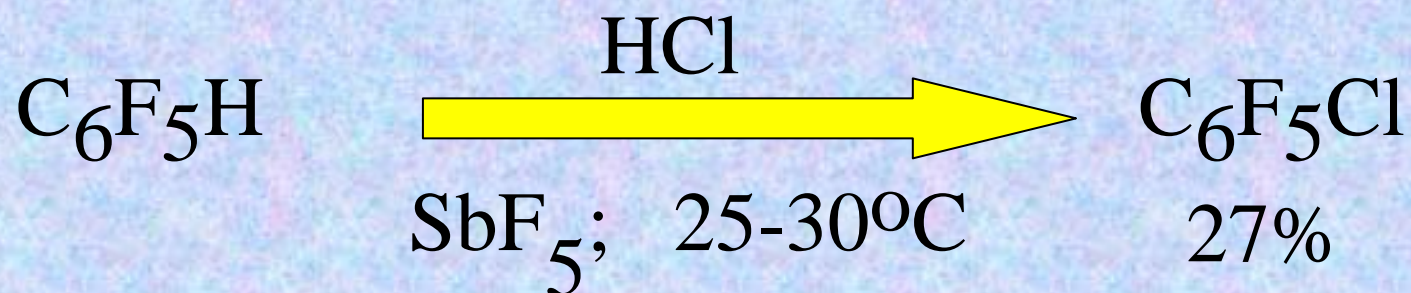
*N.N. Vorozhtsov Novosibirsk Institute of Organic
Chemistry SB RAS
9, Academician Lavrentjev Ave., Novosibirsk,
630090 Russia
e-mail: platonov@nioch.nsc.ru*



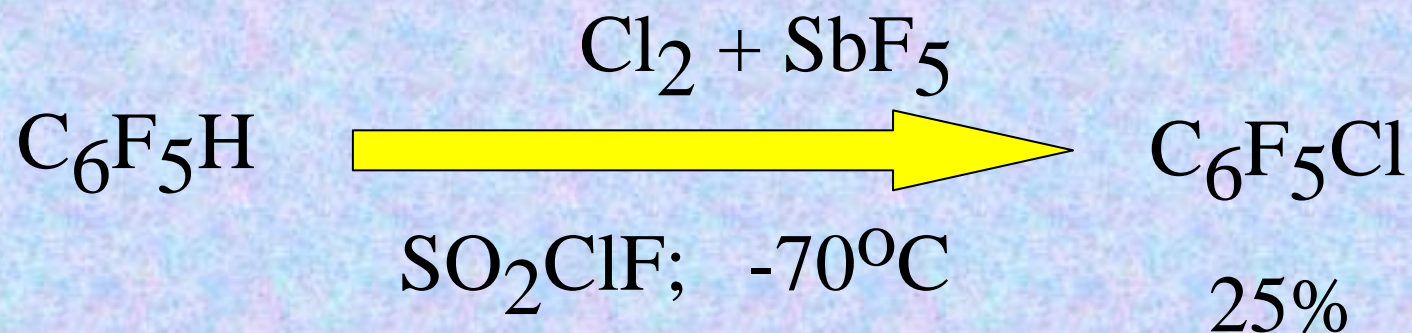
N.N.Vorozhtsov, V.E.Platonov, G.G.Yakobson,
Izv. Acad. Nauk SSSR, Ser. Khim., 1963, p.1524.



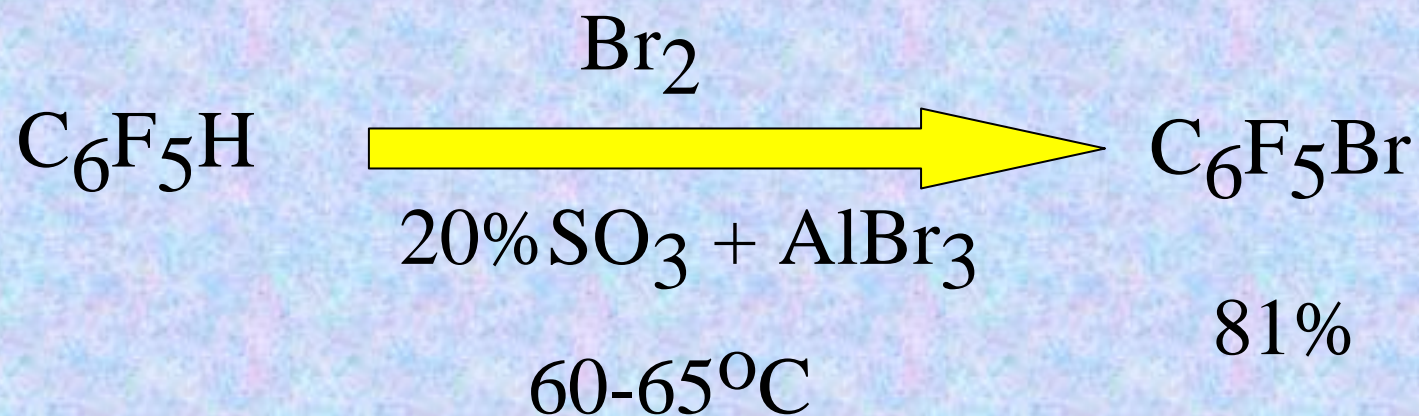
G.G.Yakobson, N.E.Mironova, A.K.Petrov, N.N.Vorozhtsov,
Zh. Obshch. Khim., 1966, vol. 36, p. 147.



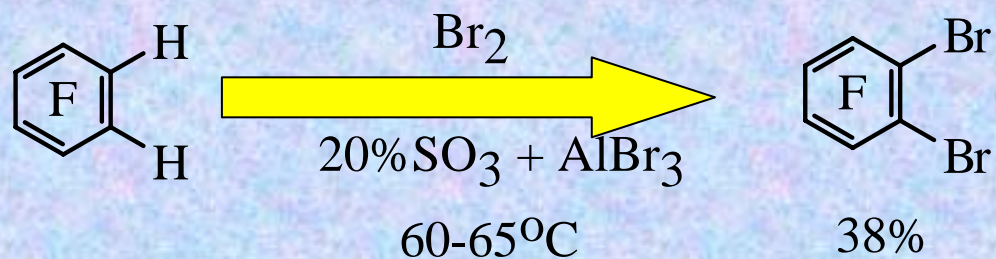
V.V.Brovko, V.A.Sokolenko, G.G.Yakobson,
Zh. Org. Khim., 1974, vol. 10, p. 300.



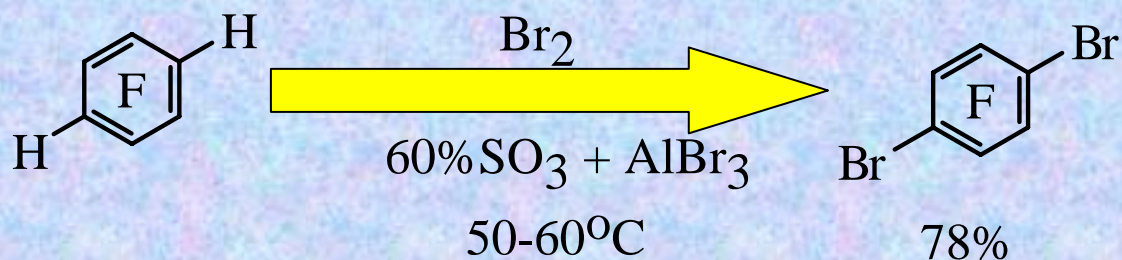
P.N.Dobronravov, V.D.Shteingarts,
Zh. Org. Khim., 1977, vol. 13, p.1679.



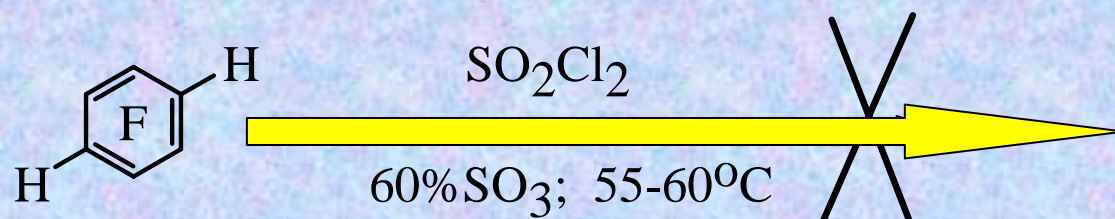
E.Nield, R.Stephens, J.C.Tatlow,
J.Chem.Soc., 1959, p. 166.



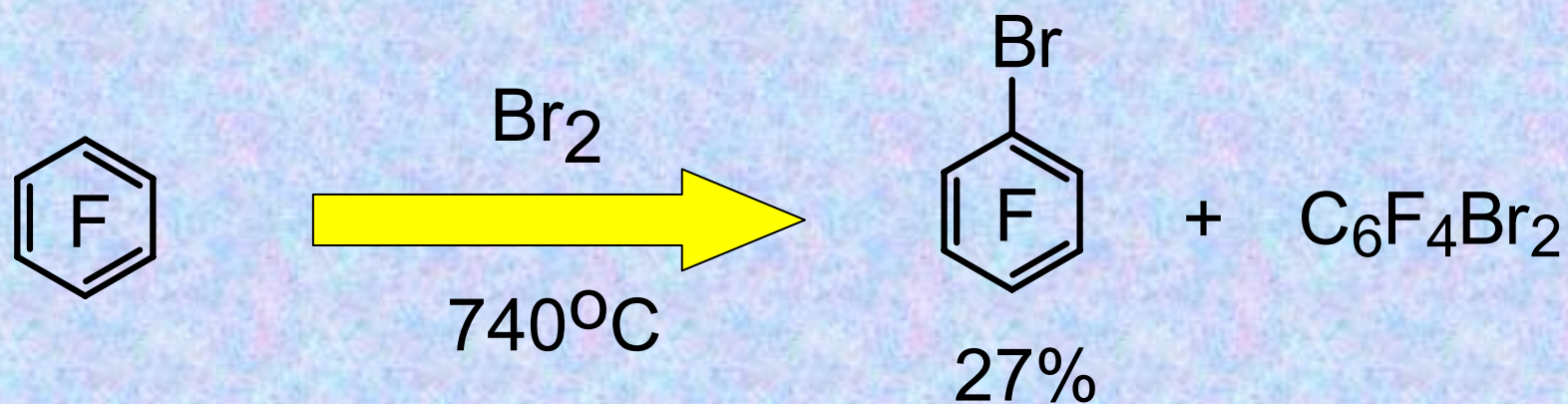
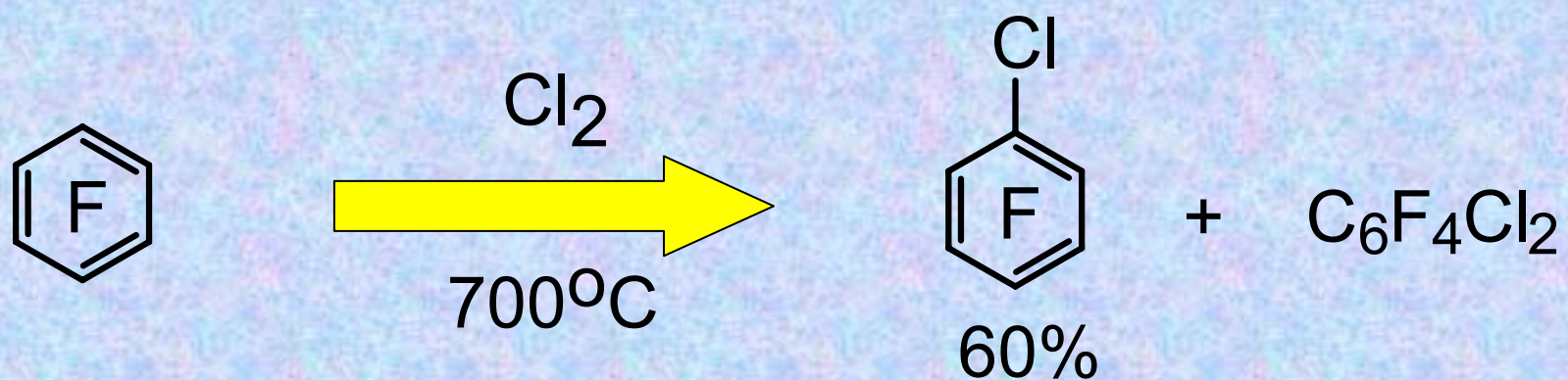
E.Nield, R.Stephens, J.C.Tatlow,
J. Chem. Soc., 1960, p.3800.



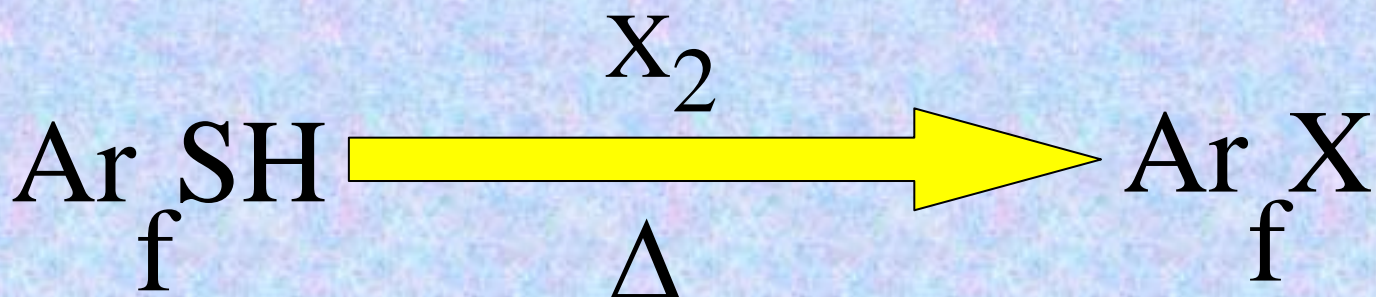
M.Hellmann, A.J.Bilbo,
J.Am.Chem.Soc., 1953, v.75, p.4590.



M.Hellmann, A.J.Bilbo, W.J.Pummer,
J.Am.Chem.Soc., 1955, v.77, p.3650.



J. Antonucci, L. Wall, J. Res. NBS., 1966, vol.70a, p.473.



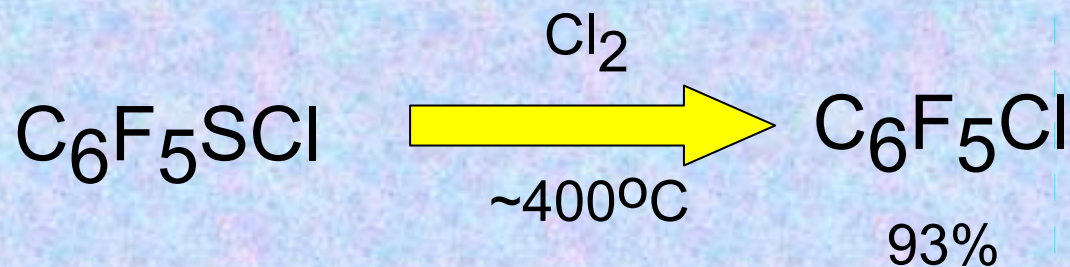
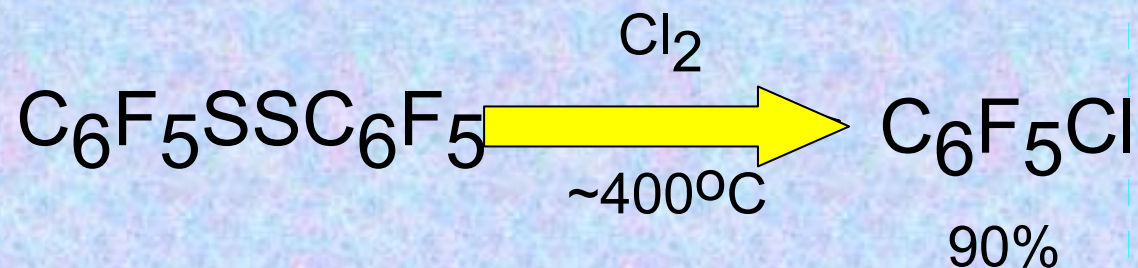
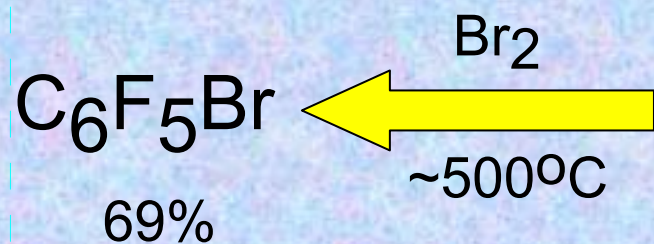
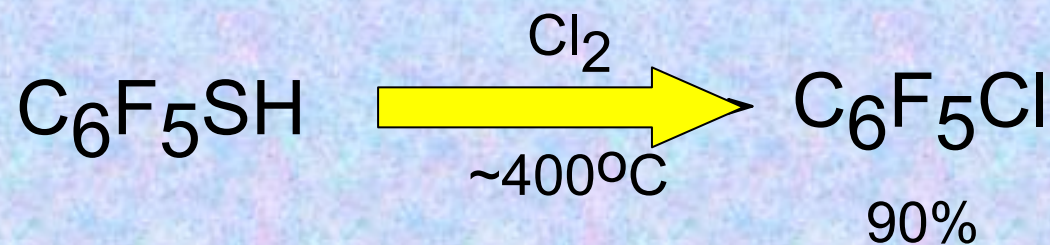
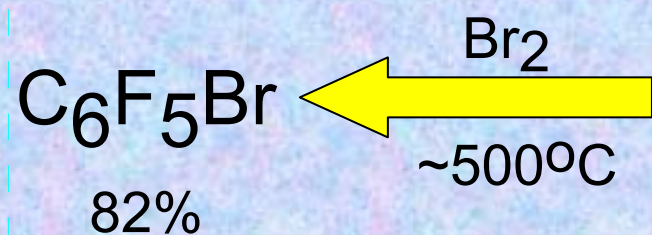
$\text{X} = \text{Cl} (400^\circ\text{C}); \text{Br} (500^\circ\text{C})$

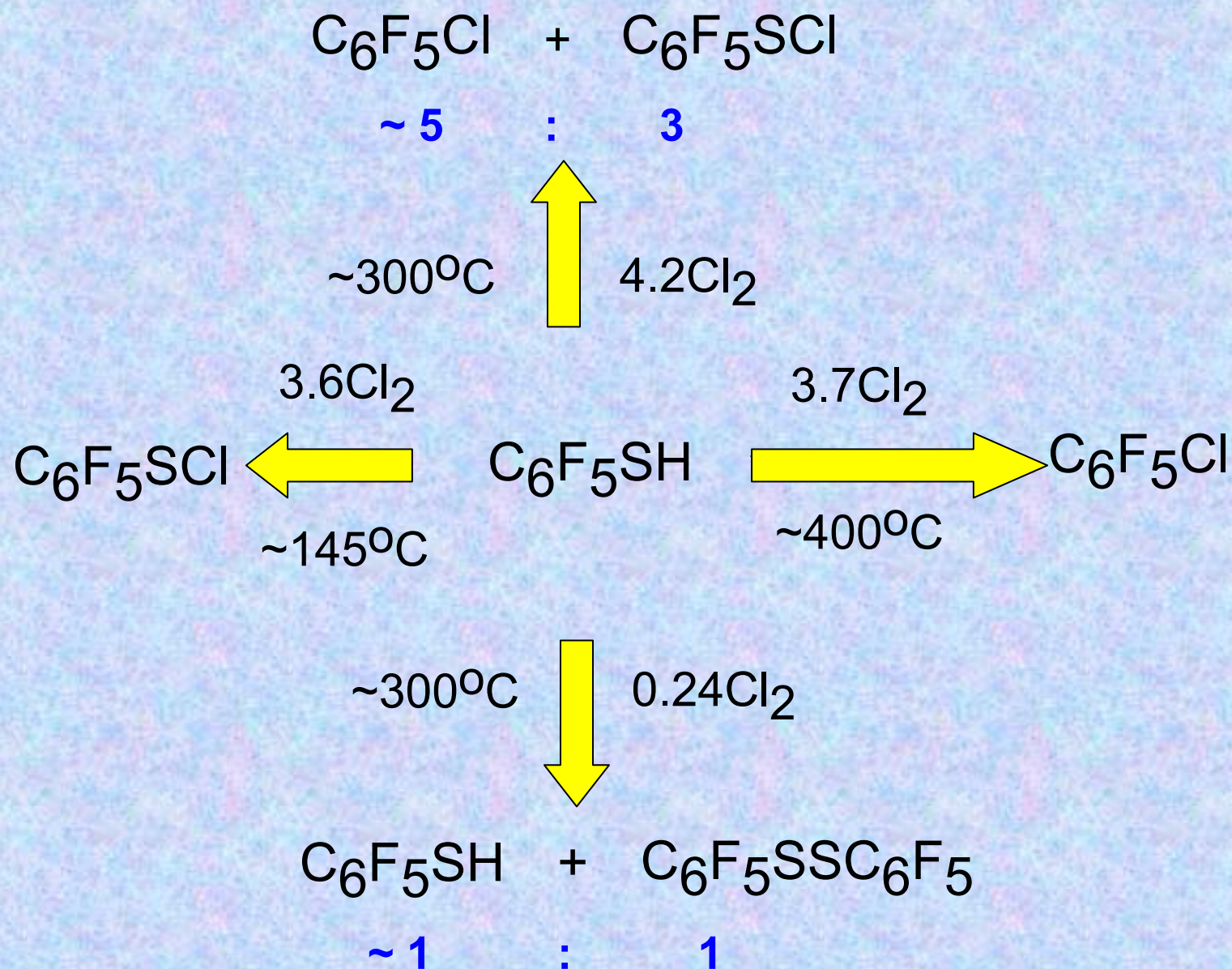
Flow system

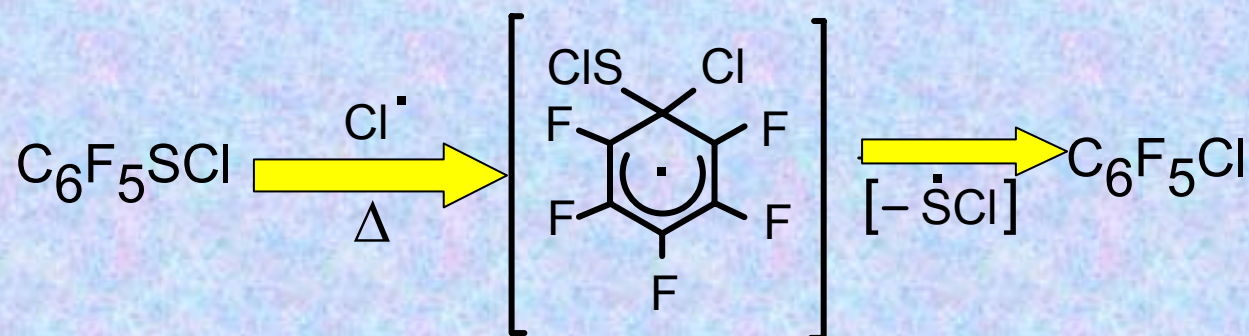
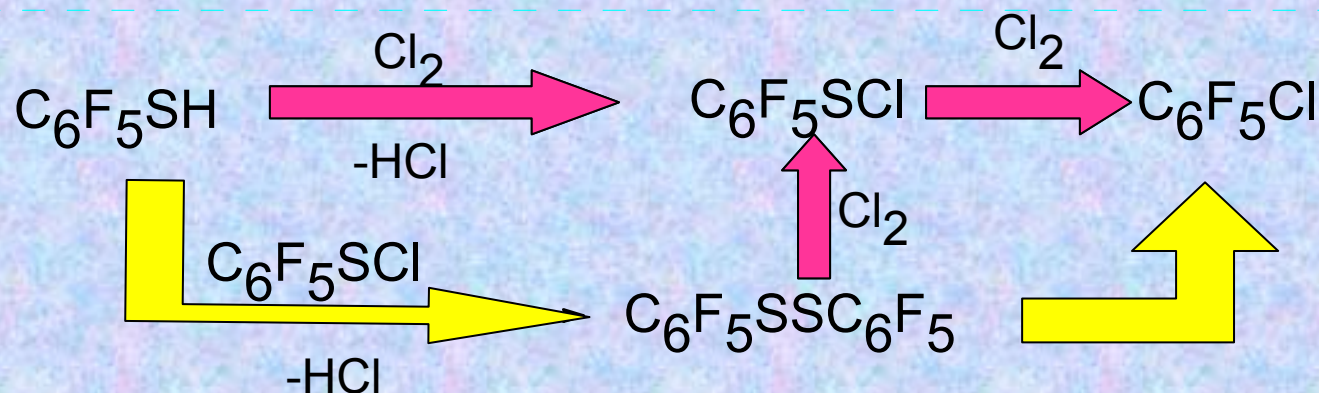
Yields of the target products

Cl (84-95%), Br (68-91%)

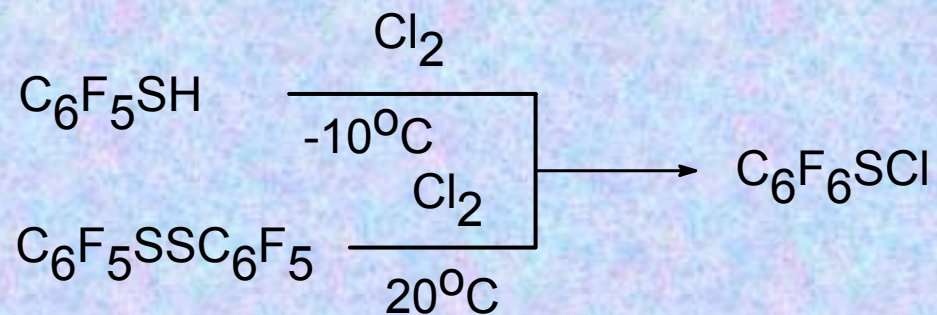
Purity of the crude reaction products 96-99%

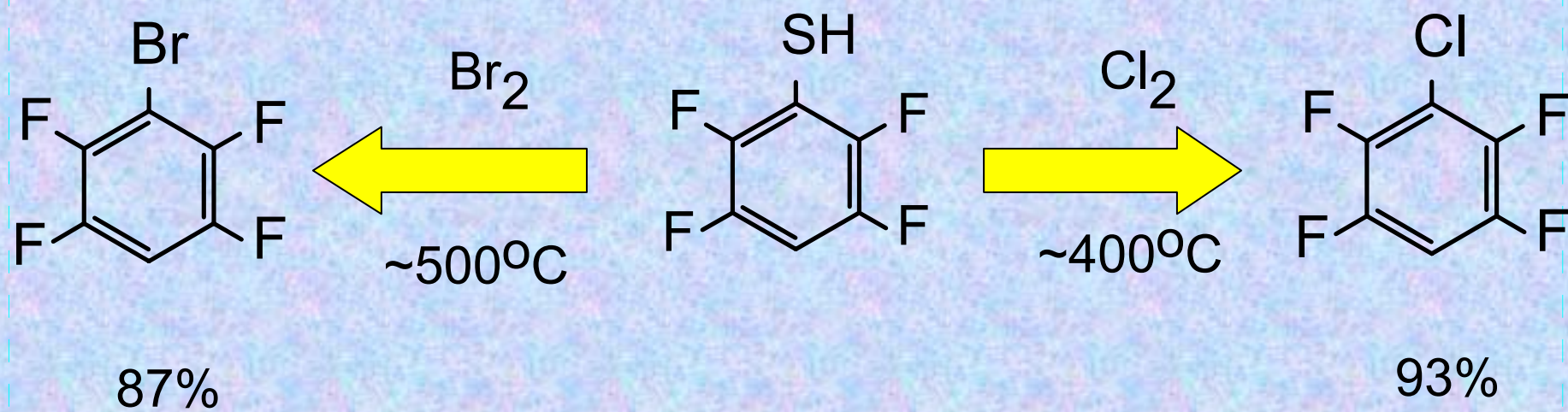


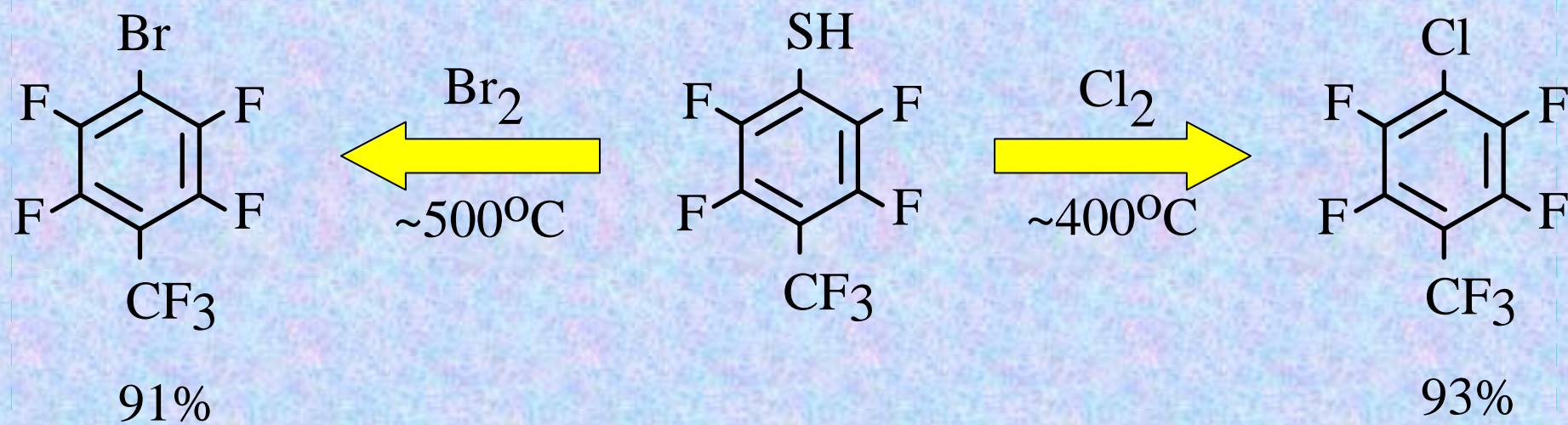


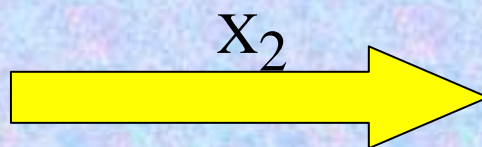
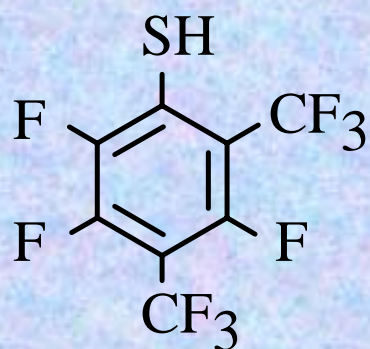


P.Sartori, A.Golloch, Chem. Ber., 1970, b.103, 3936.

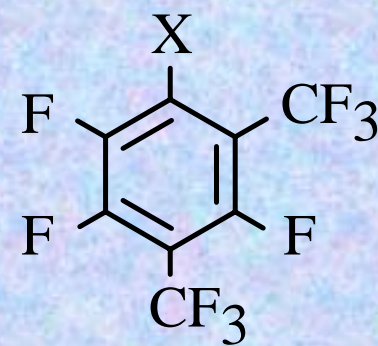




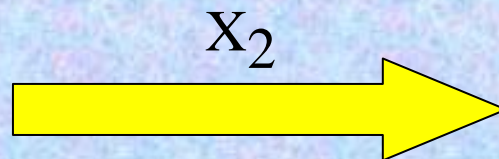
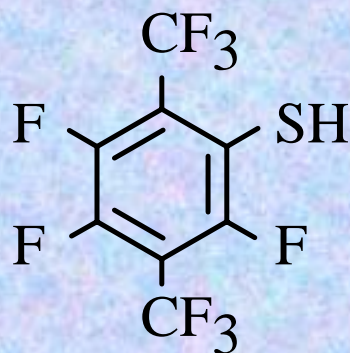




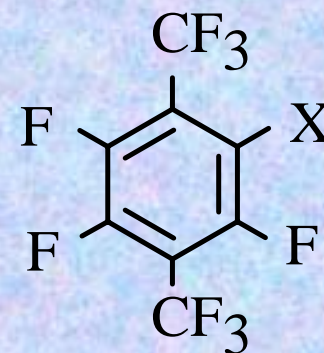
X = Cl (400°C)
Br (500°C)



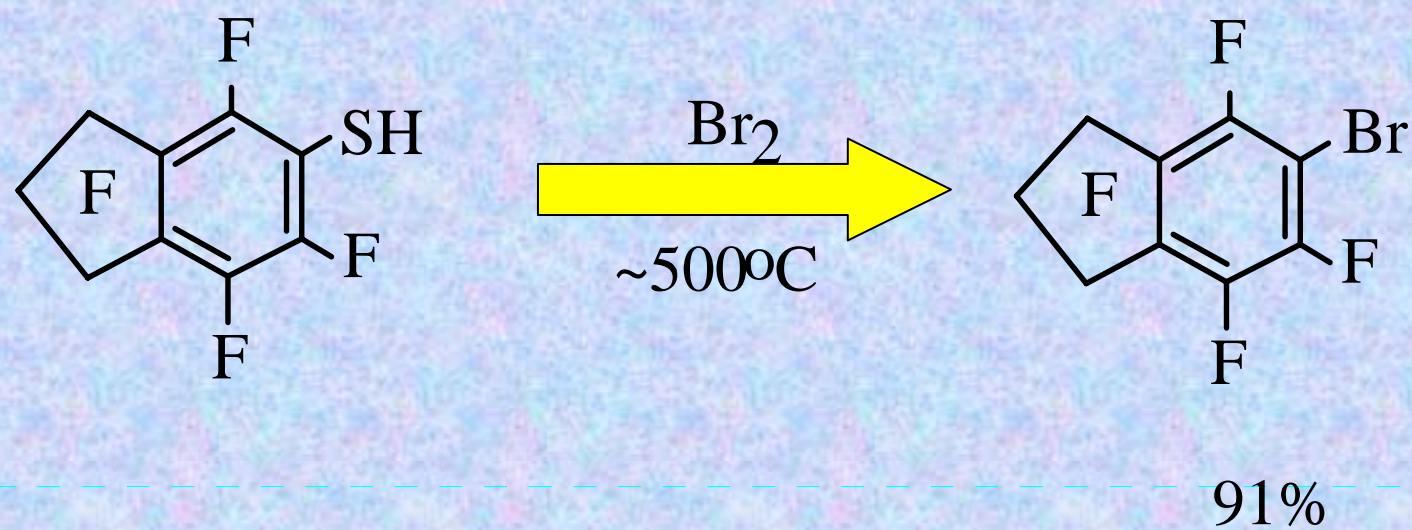
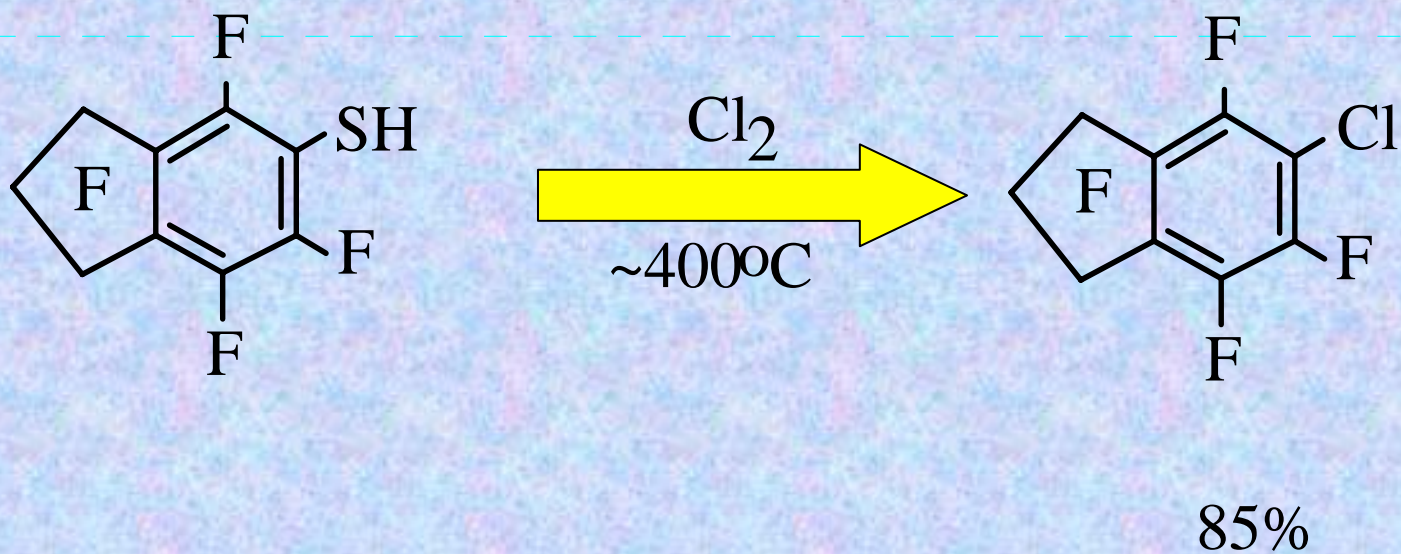
93%
87%

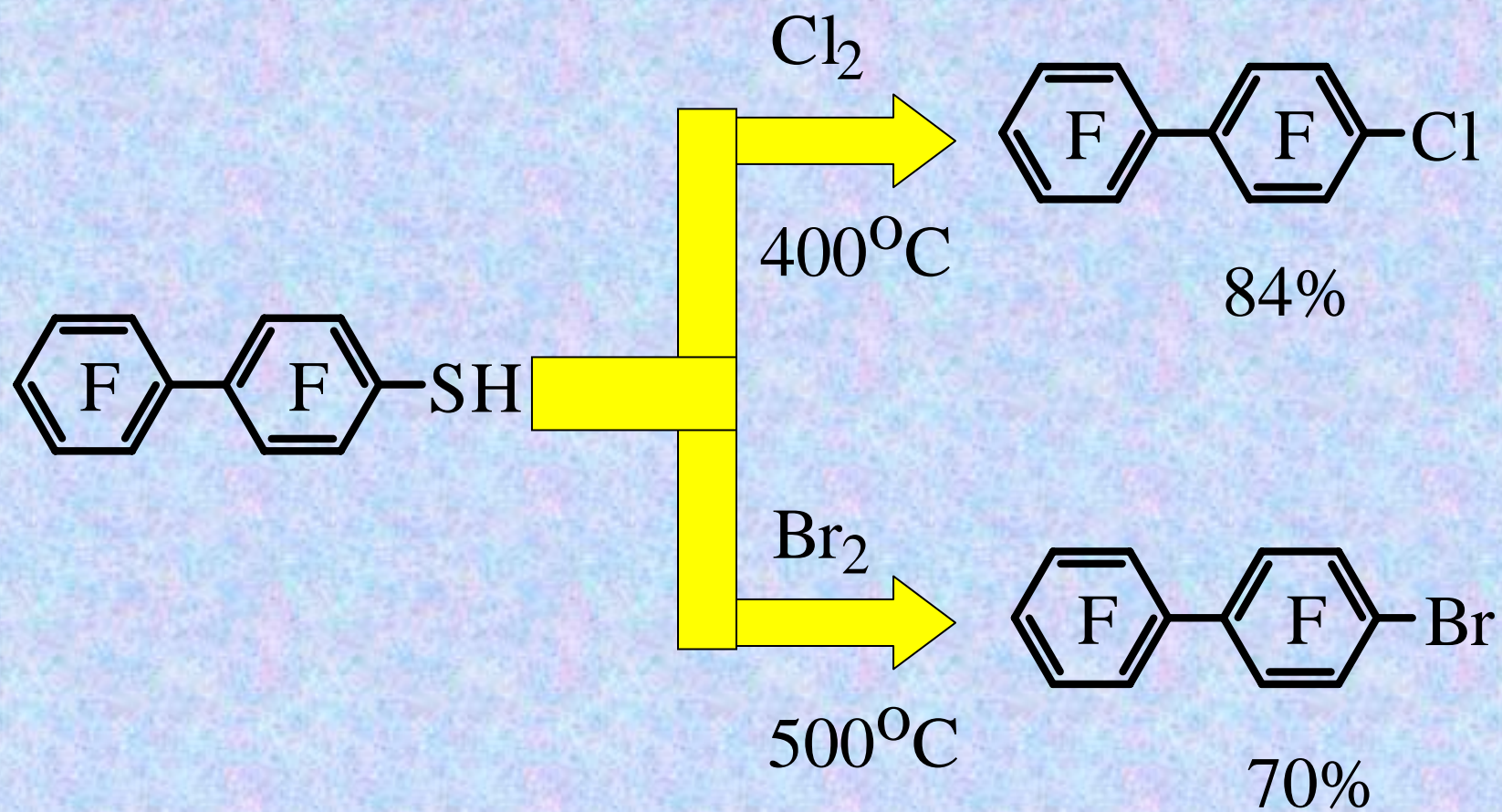


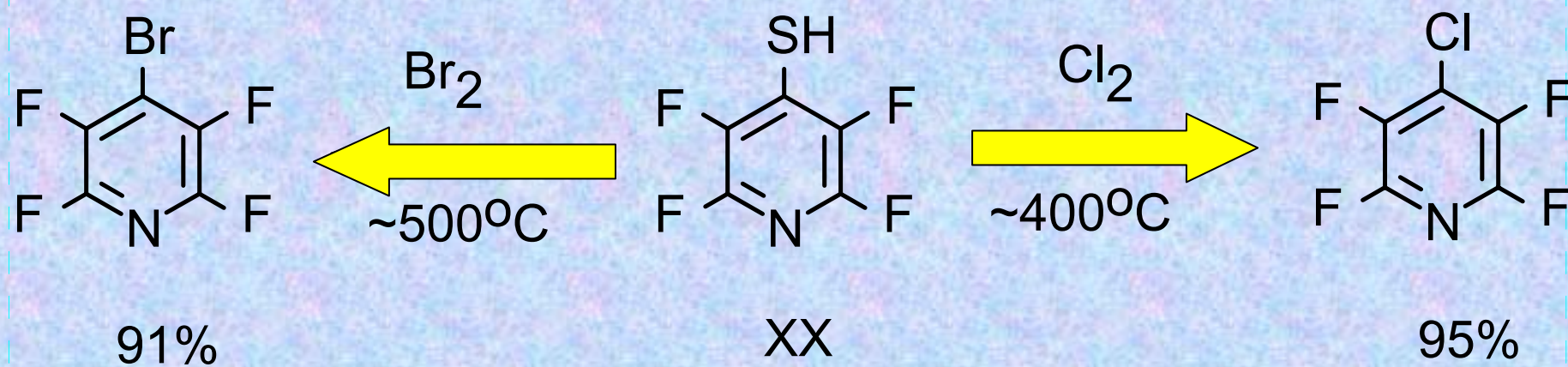
X = Cl (400°C)
Br (500°C)

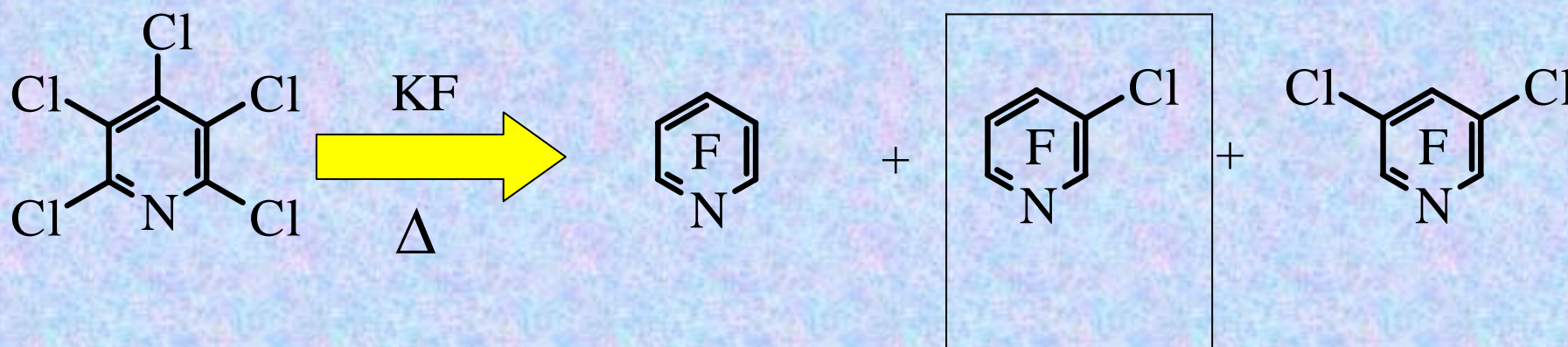


84%
68%





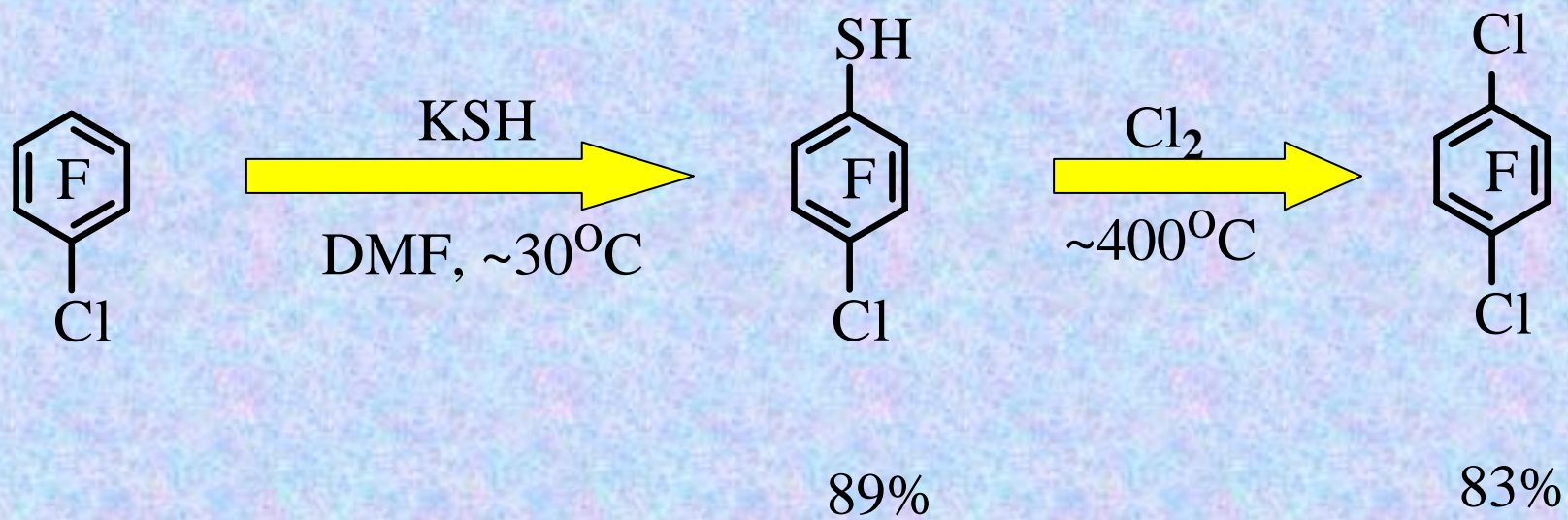


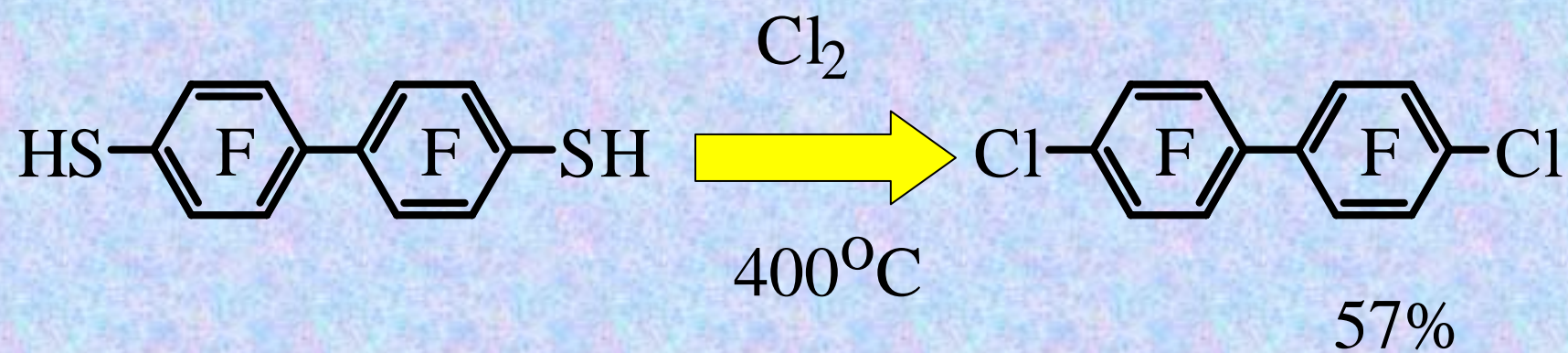


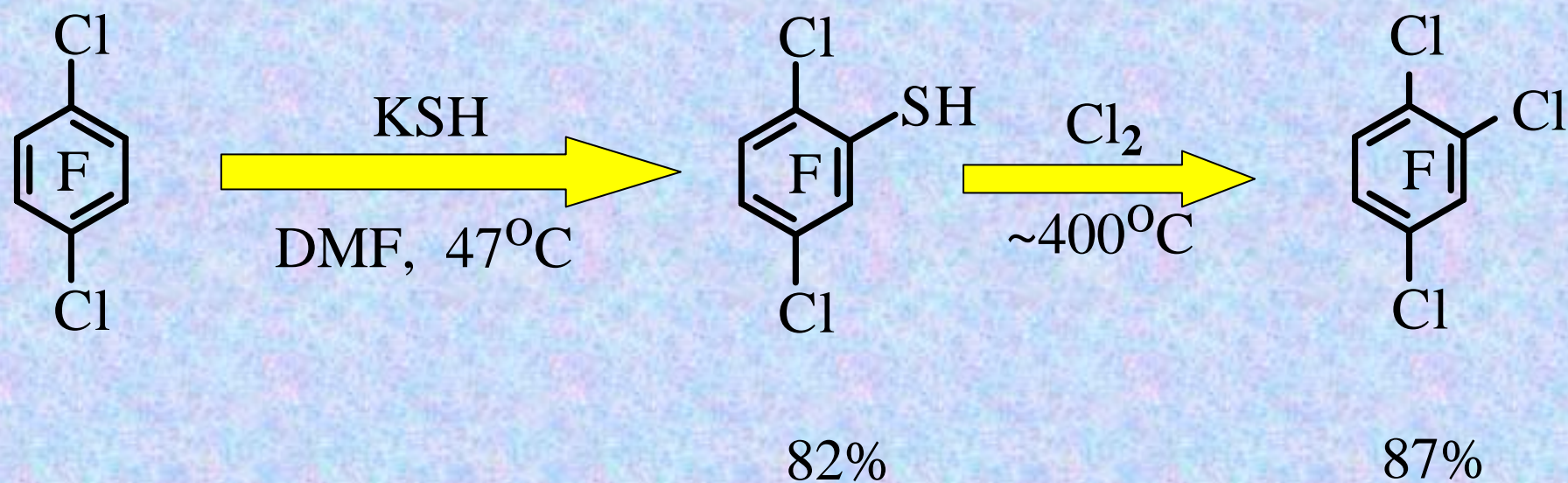
450-480°C (autoclave)

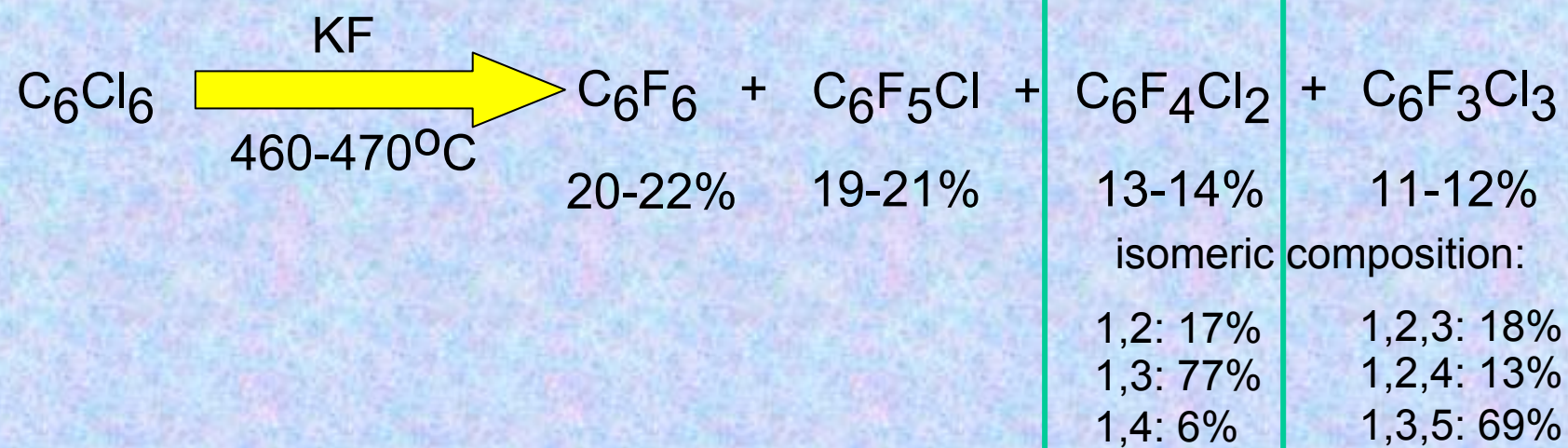
R.D.Chambers, J.Hutchinson, W.K.R.Musgrave,
J.Chem.Soc., 1964, p.3573

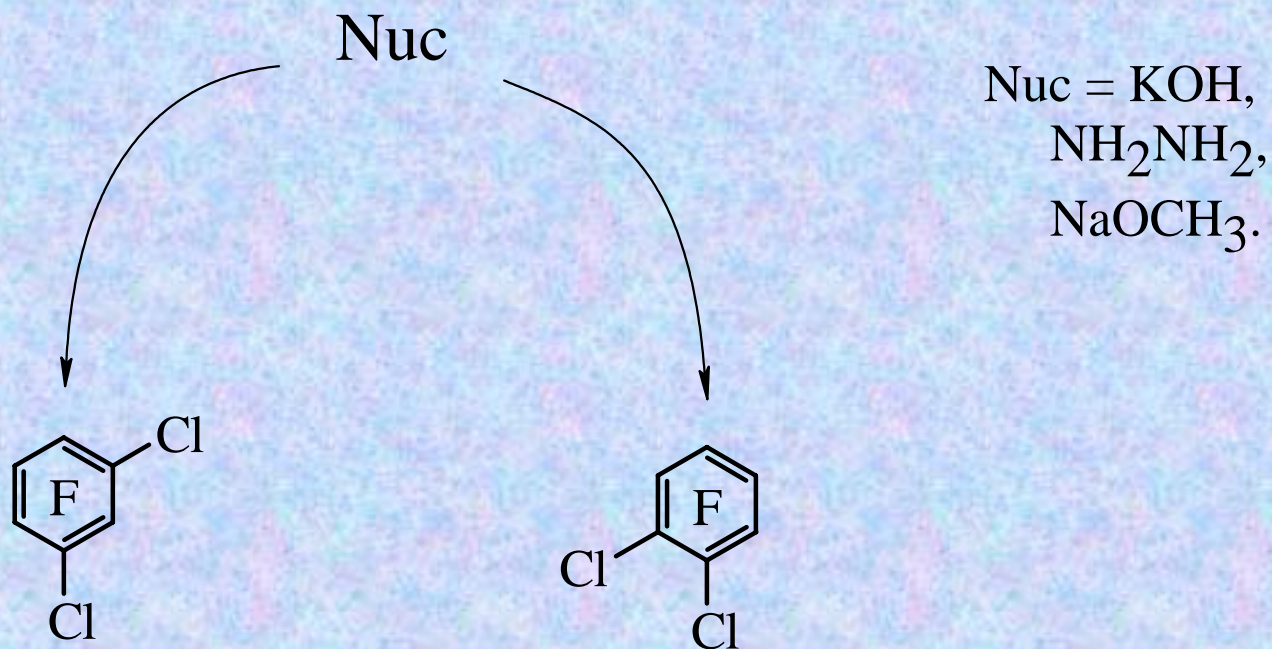
R.E.Banks, R.N.Haszeldine, J.V.Latham, I.M.Young,
Chem.and Ind., 1964, p.835.



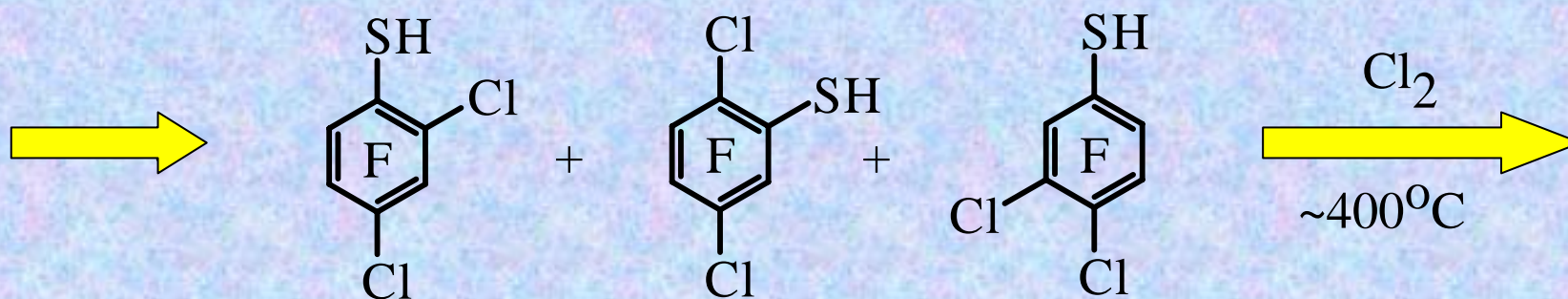
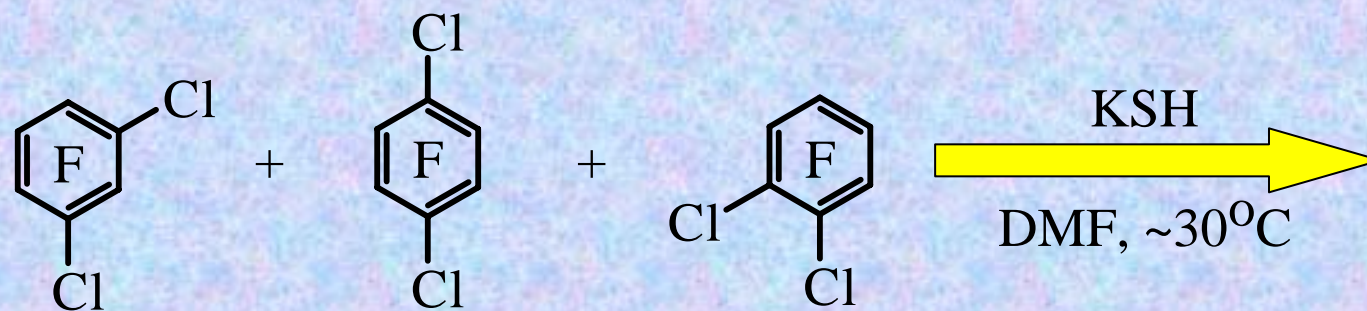




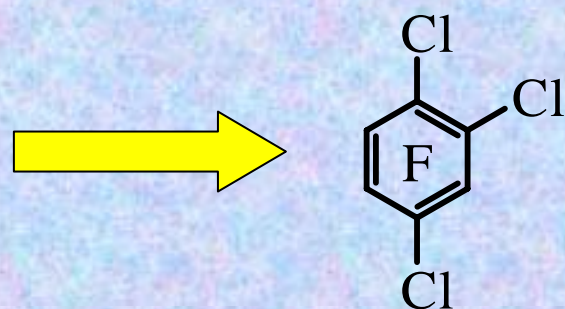




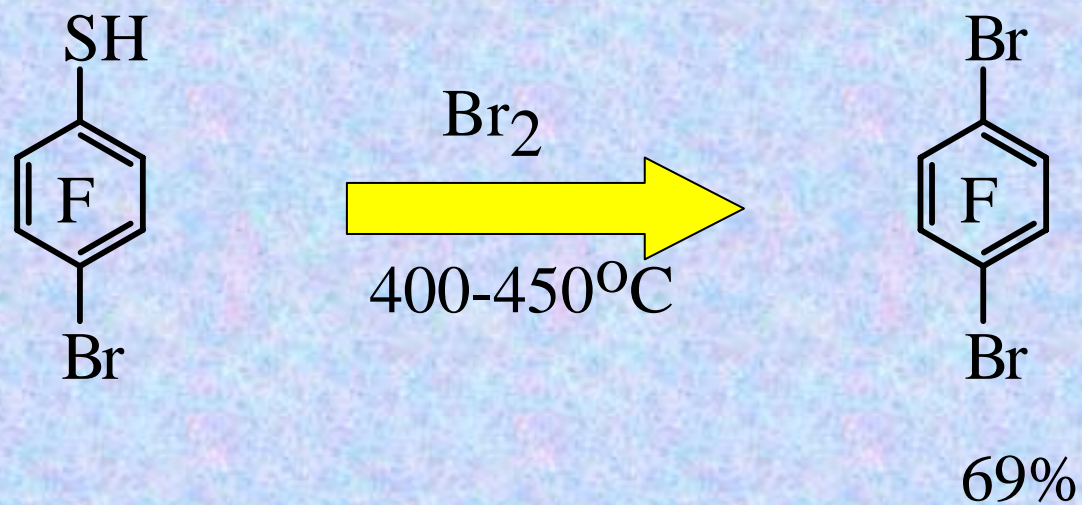
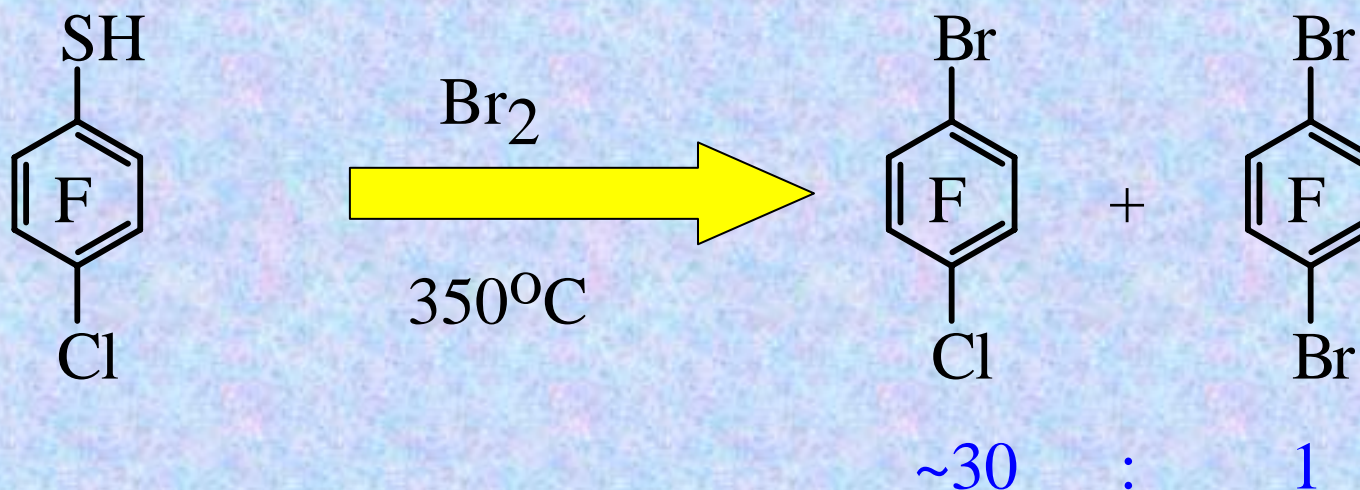
1. G.P.Tataurov, L.N.Pushkina, N.I.Gubkina, V.F.Kollegov, S.V.Sokolov, Zh. Obshch. Khim., 1967, v.37, p.674.
2. N.Ichikawa, S.Hayaski, Nippon Kagaku Zasshi, 1968, v.89(3), p.321; Chem. Abstr., 1968, v. 69, p.67021.
3. R.D.Chambers, D.Close, D.L.H.Williams, J. Chem. Soc., 1980, p.778.



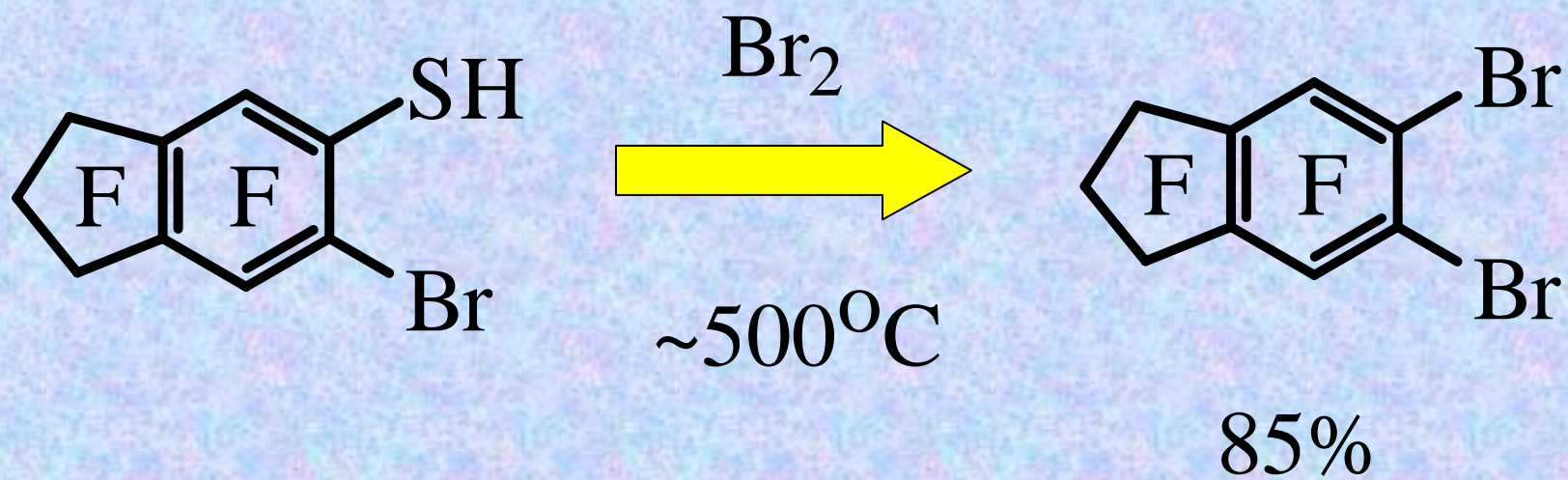
total yield $\sim 85\%$

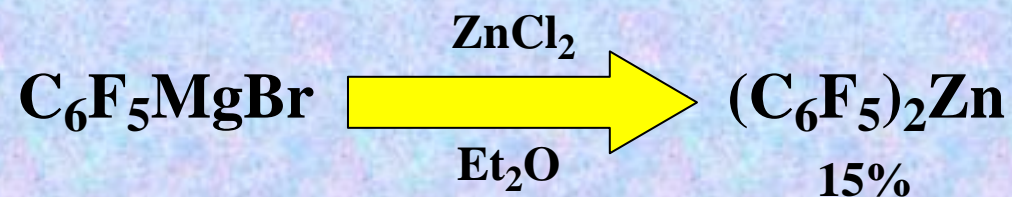


$\sim 86\%$

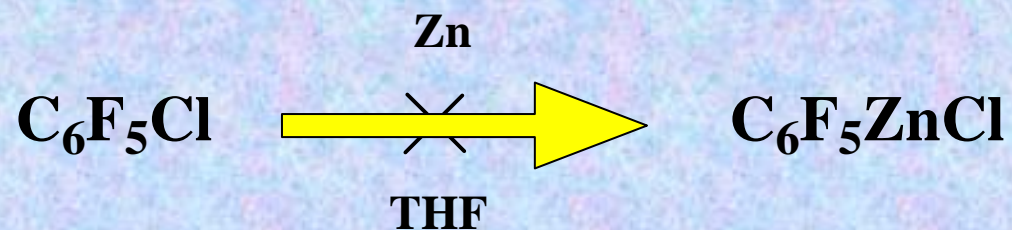
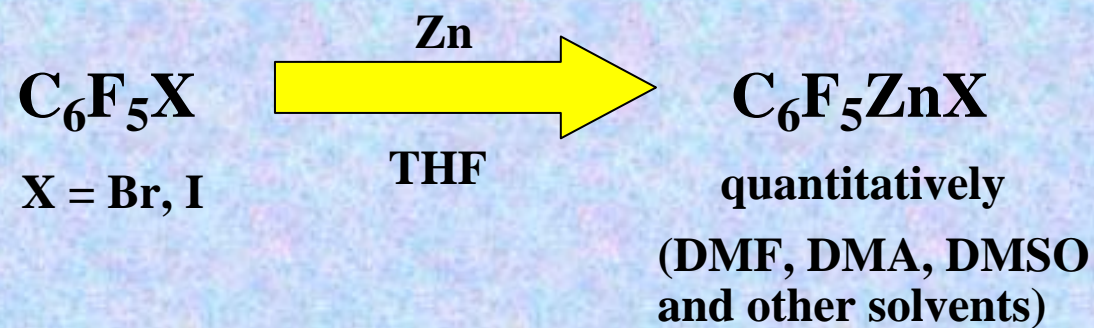


Purity of the crude reaction product - 99%

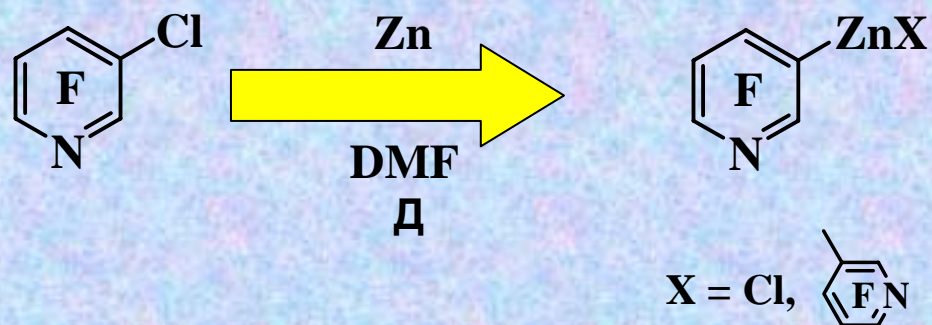
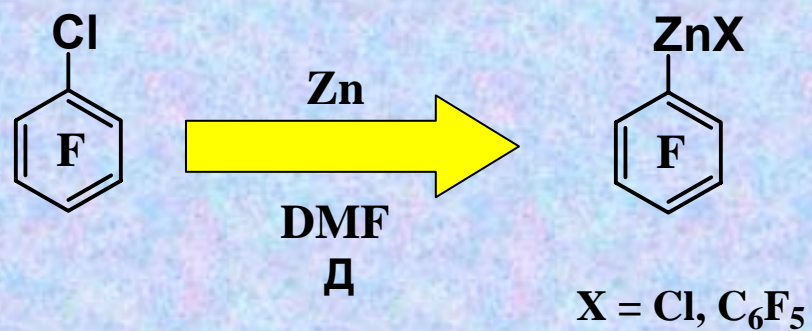




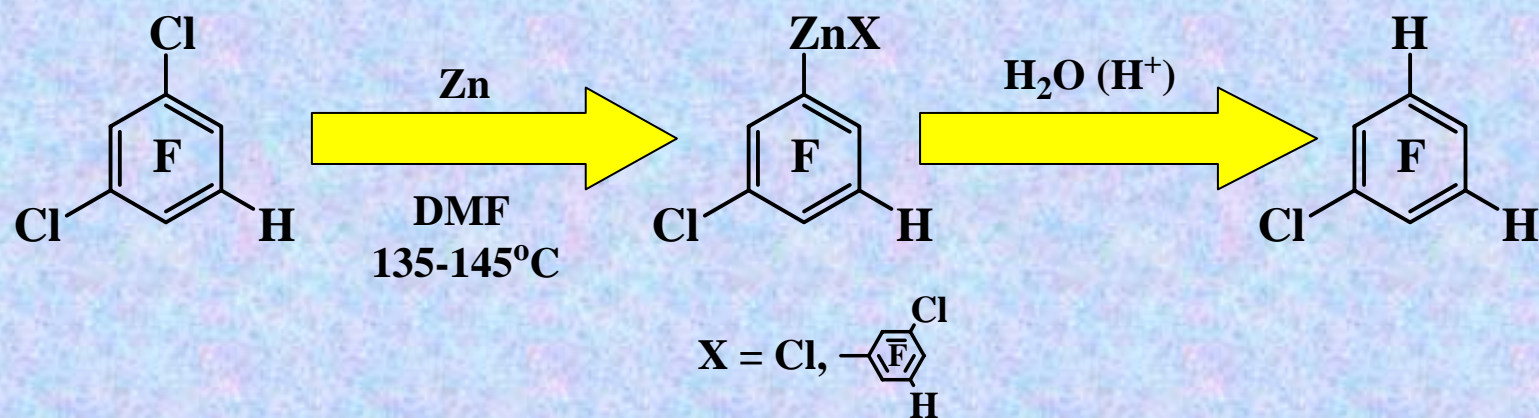
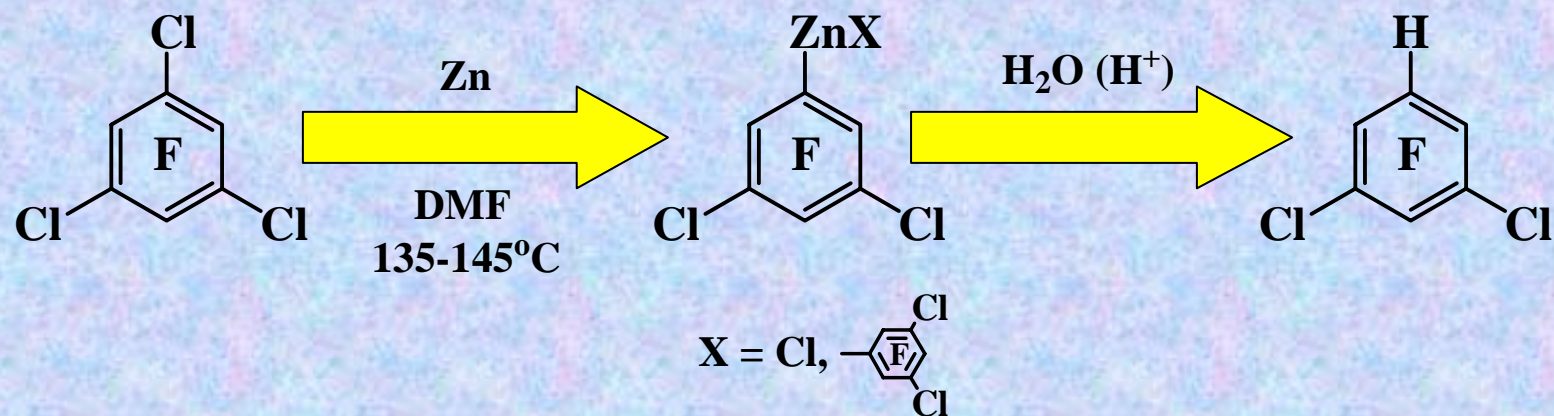
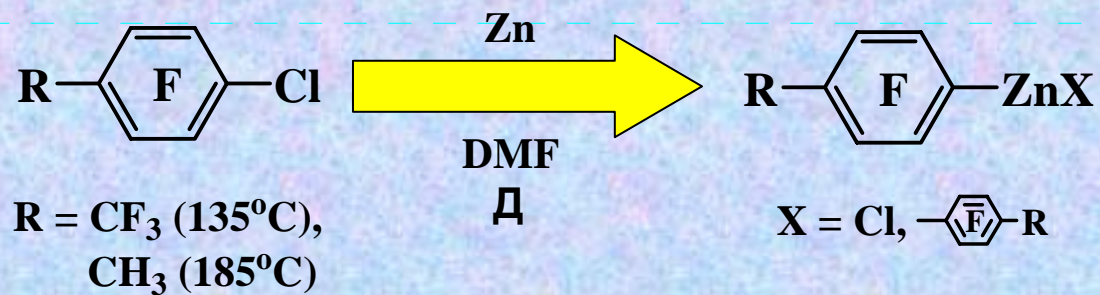
J.G. Noltes, J.W.G. Van den Hurk. J. Organometal. Chem., 1964, vol.1, p.377.



D.E. Evans, R.F. Phillips. J. Chem. Soc., Dalton Trans., 1973, p.978.



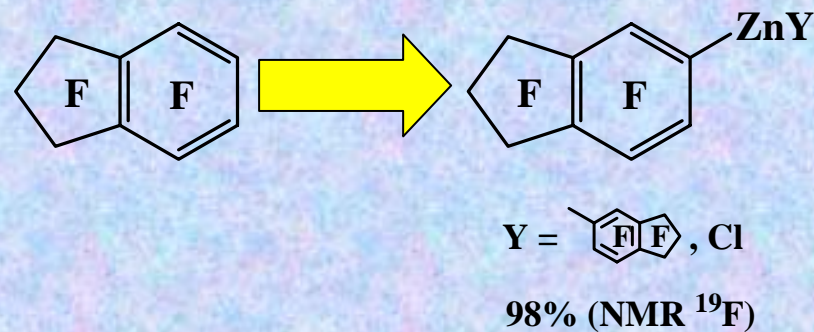
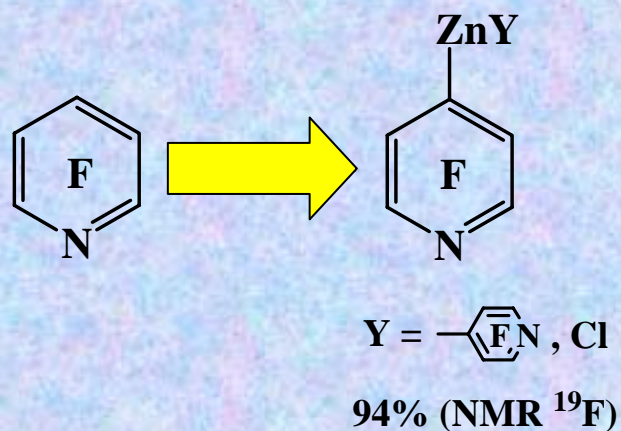
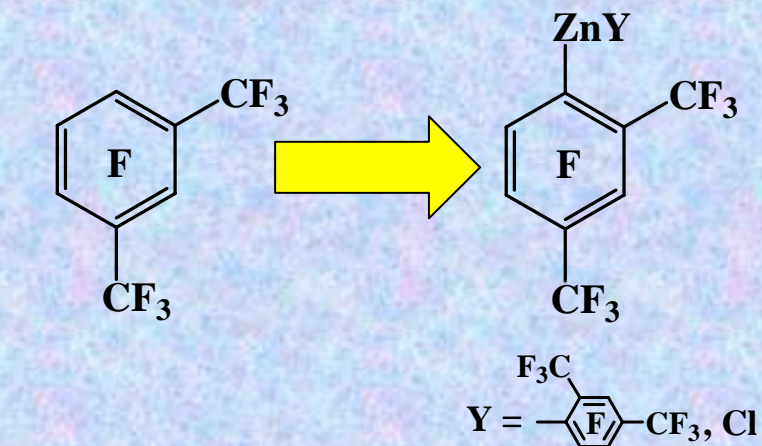
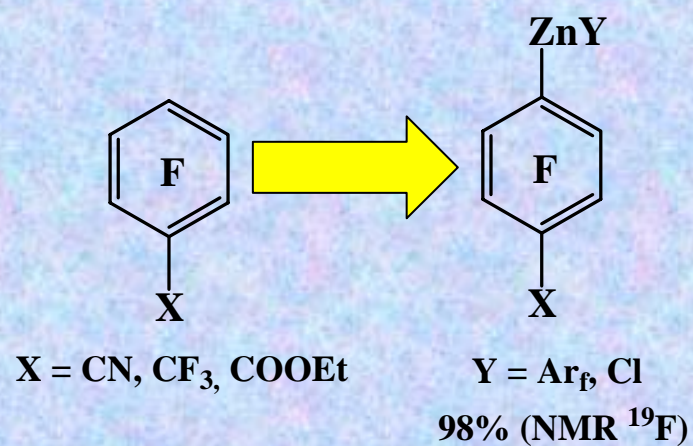
V.I. Krasnov, V.E. Platonov. Presented at the Xth International Symposium on Fluorine Chemistry, Padua, Italy, 1992, paper C19; V.I. Krasnov, V.E. Platonov. J. Fluorine Chem., 1992, vol.58, p.246.



1) V.I. Krasnov, V.E. Platonov. Zh. Org. Khim., 2000, vol.36, p.1524.

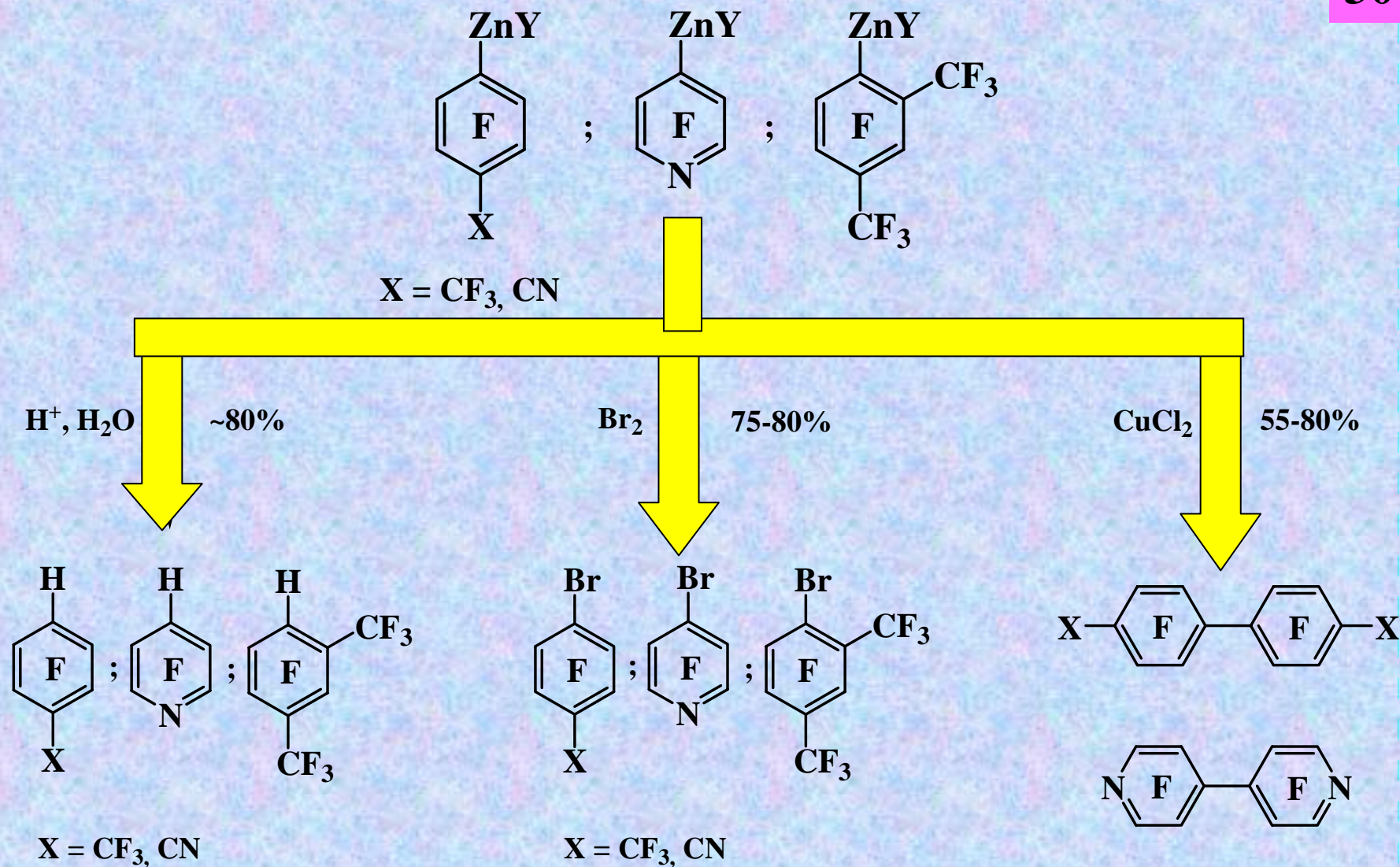
2) A.S. Vinogradov, V.I. Krasnov, V.E. Platonov. Zh. Org. Khim., 2006, in press.

Zn / SnCl₂ / DMF, 20-65°C, 5-24 h

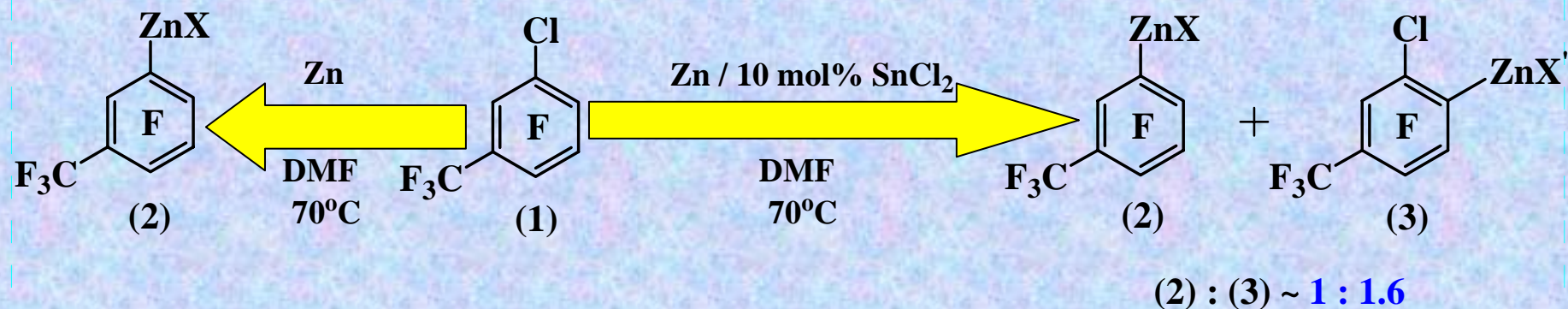


1) A.O. Miller, V.I. Krasnov, D. Peters, V.E. Platonov, R. Miethchen. *Tetrahedron Lett.*, 2000, vol.41, p.3817.

2) A.S. Vinogradov, V.I. Krasnov, V.E. Platonov. *Zh. Org. Khim.*, 2006, in press.

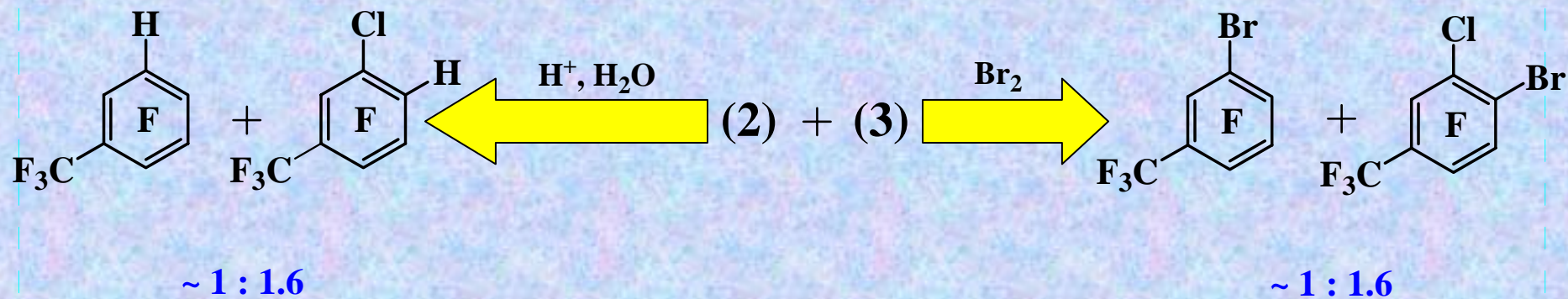


A.O. Miller, V.I. Krasnov, D. Peters, V.E. Platonov, R. Miethchen. *Tetrahedron Lett.*, 2000, vol.41, p.3817.

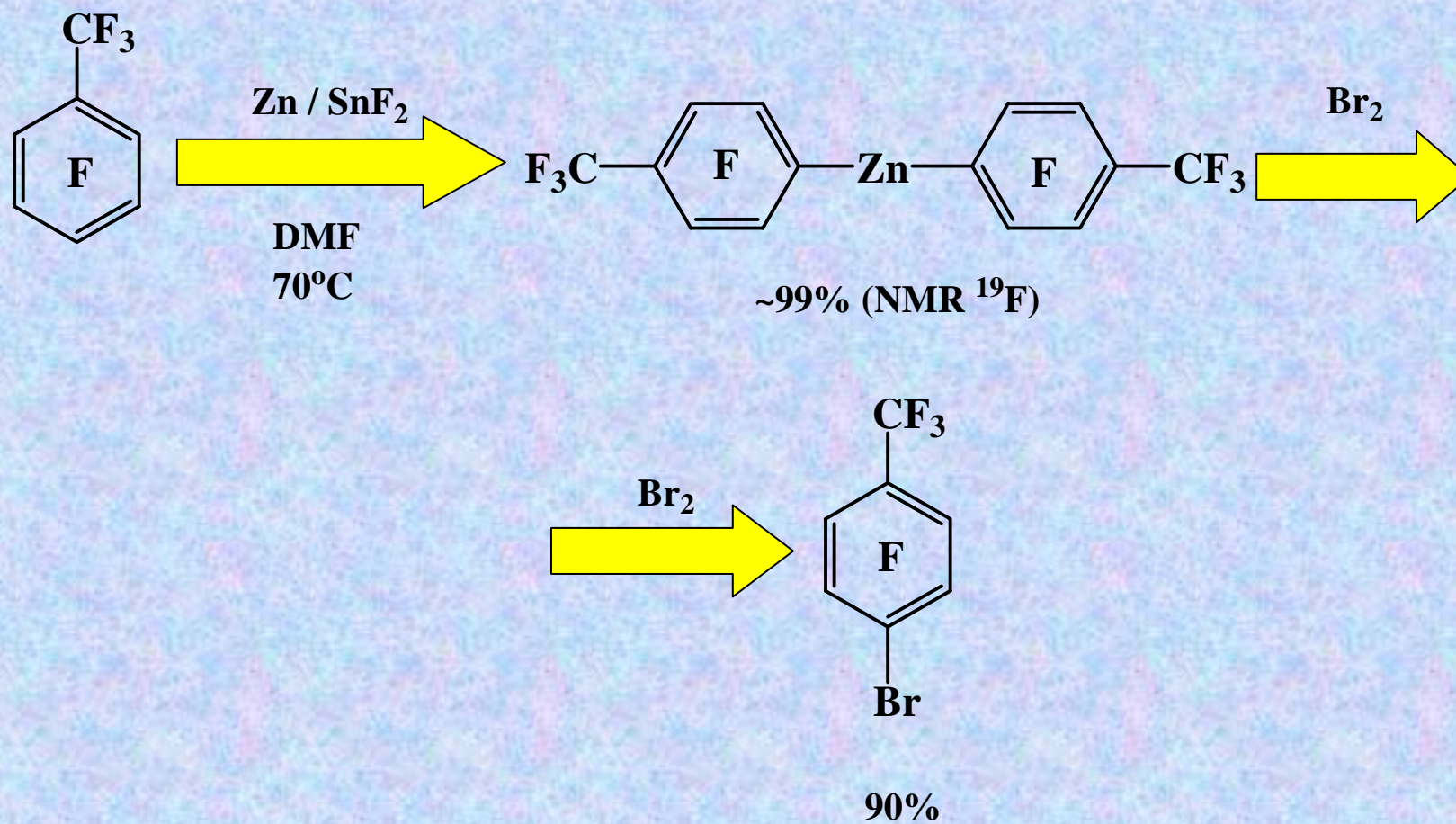


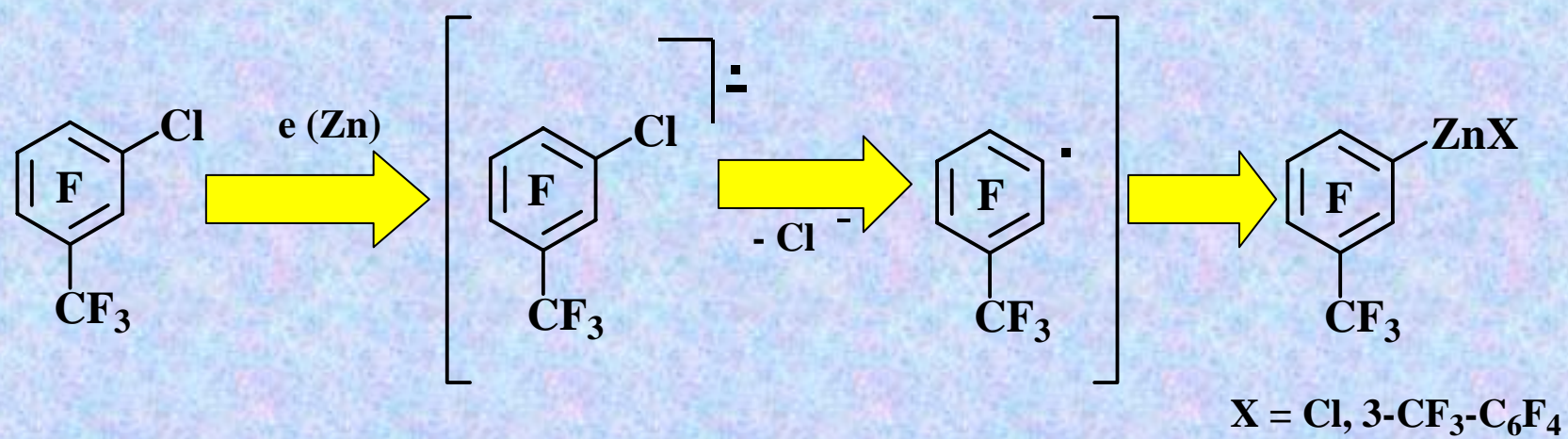
$X = \text{Cl}, 3\text{-CF}_3\text{-C}_6\text{F}_4$

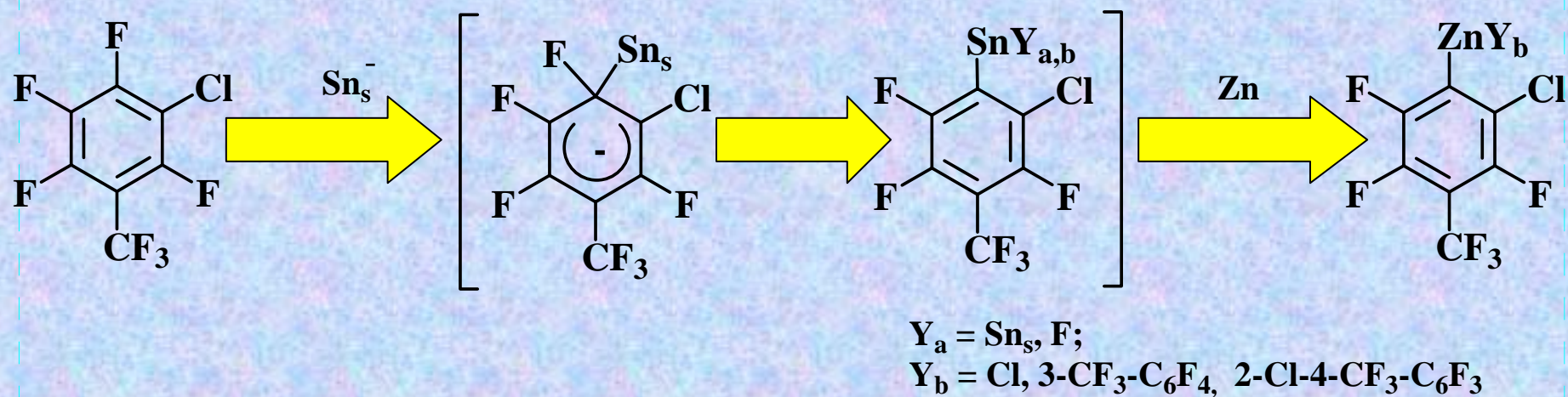
$X' = \text{Cl}, 3\text{-CF}_3\text{-C}_6\text{F}_4,$
 $2\text{-Cl-4-CF}_3\text{-C}_6\text{F}_4$



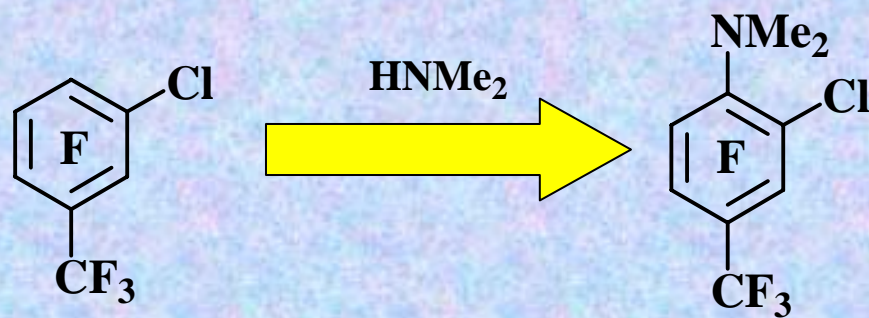
V.I. Krasnov, A.S. Vinogradov, V.E. Platonov. Mendeleev Commun., 2006, in press.

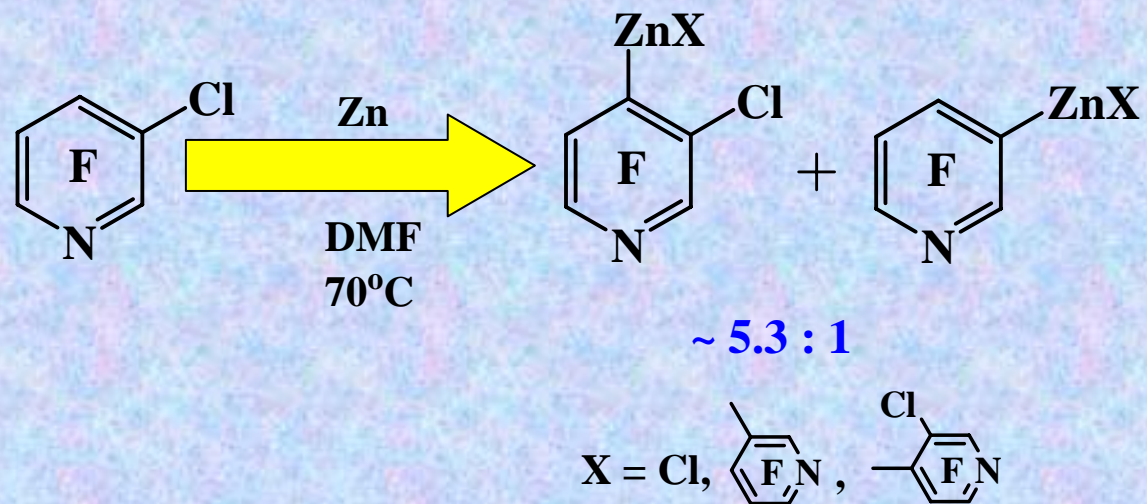
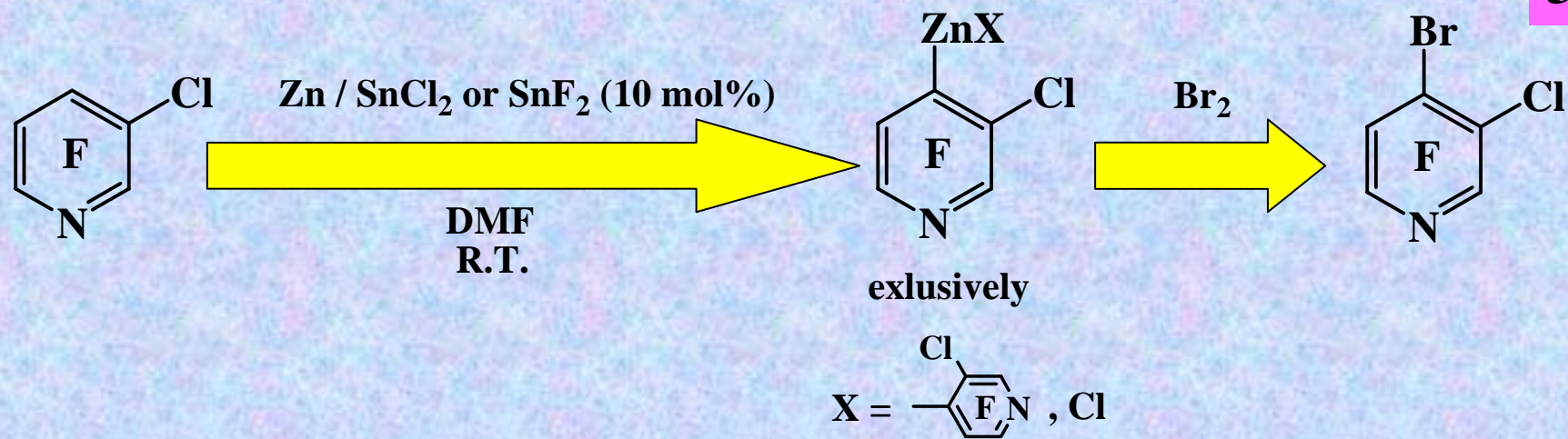


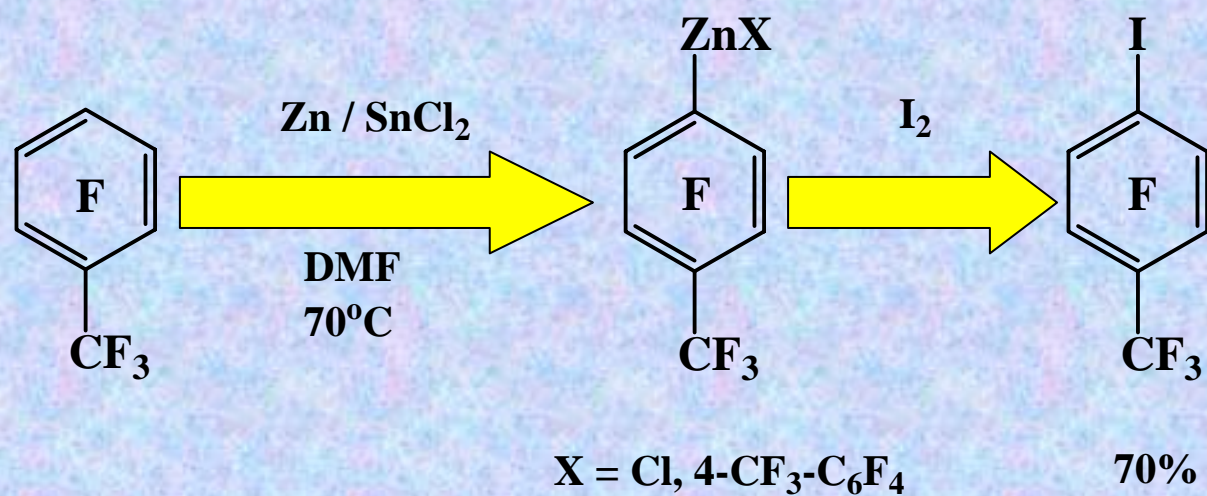
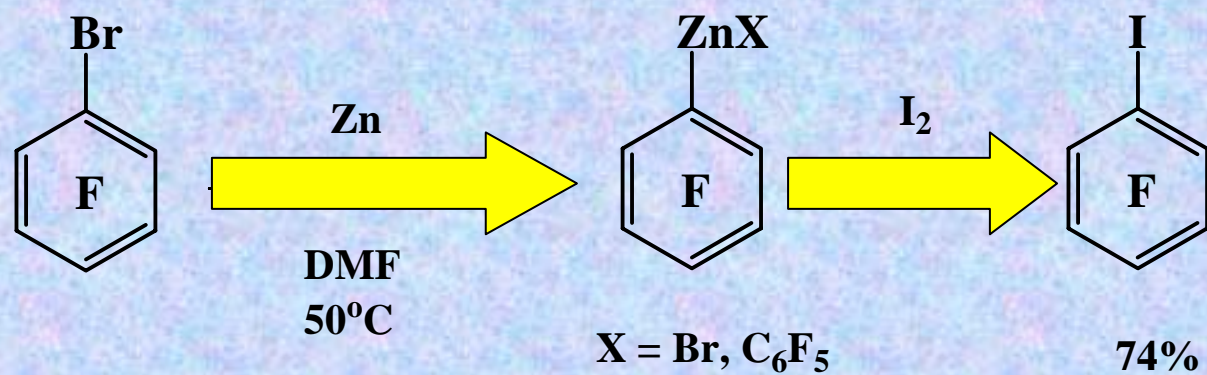


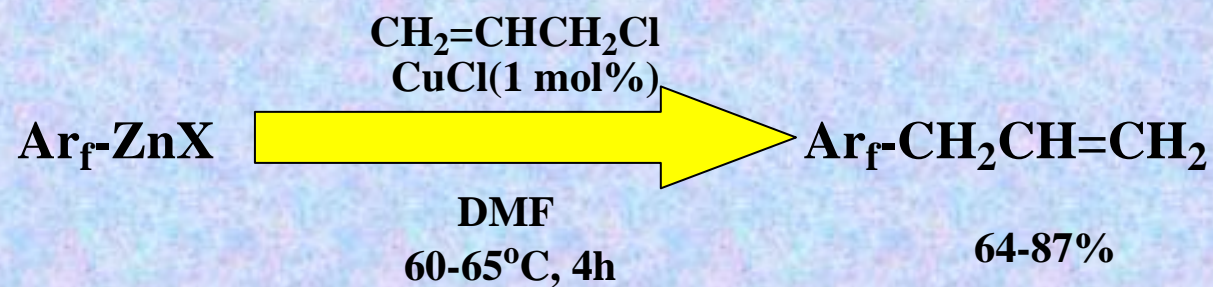
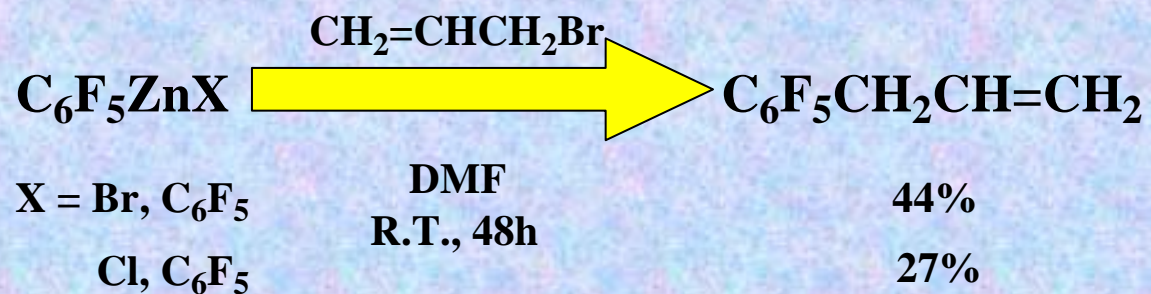


The orientation in nucleophilic substitution:

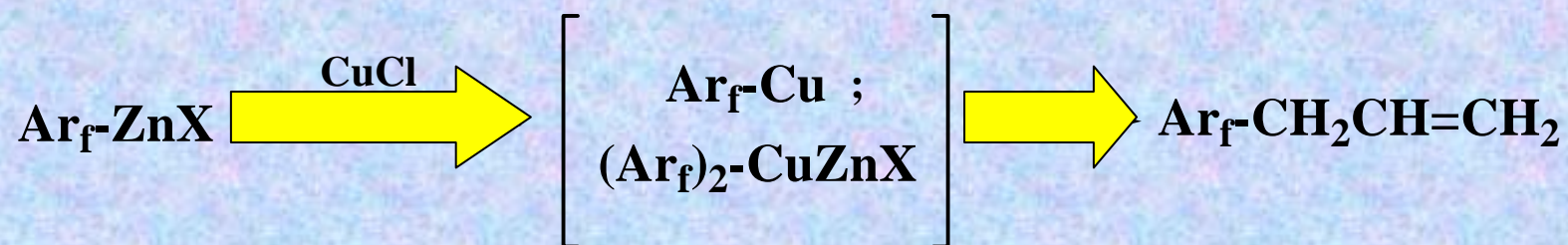
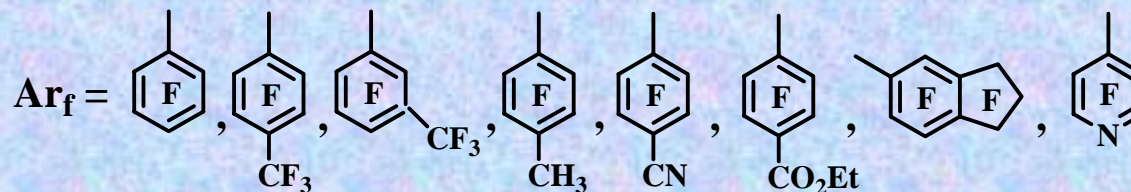


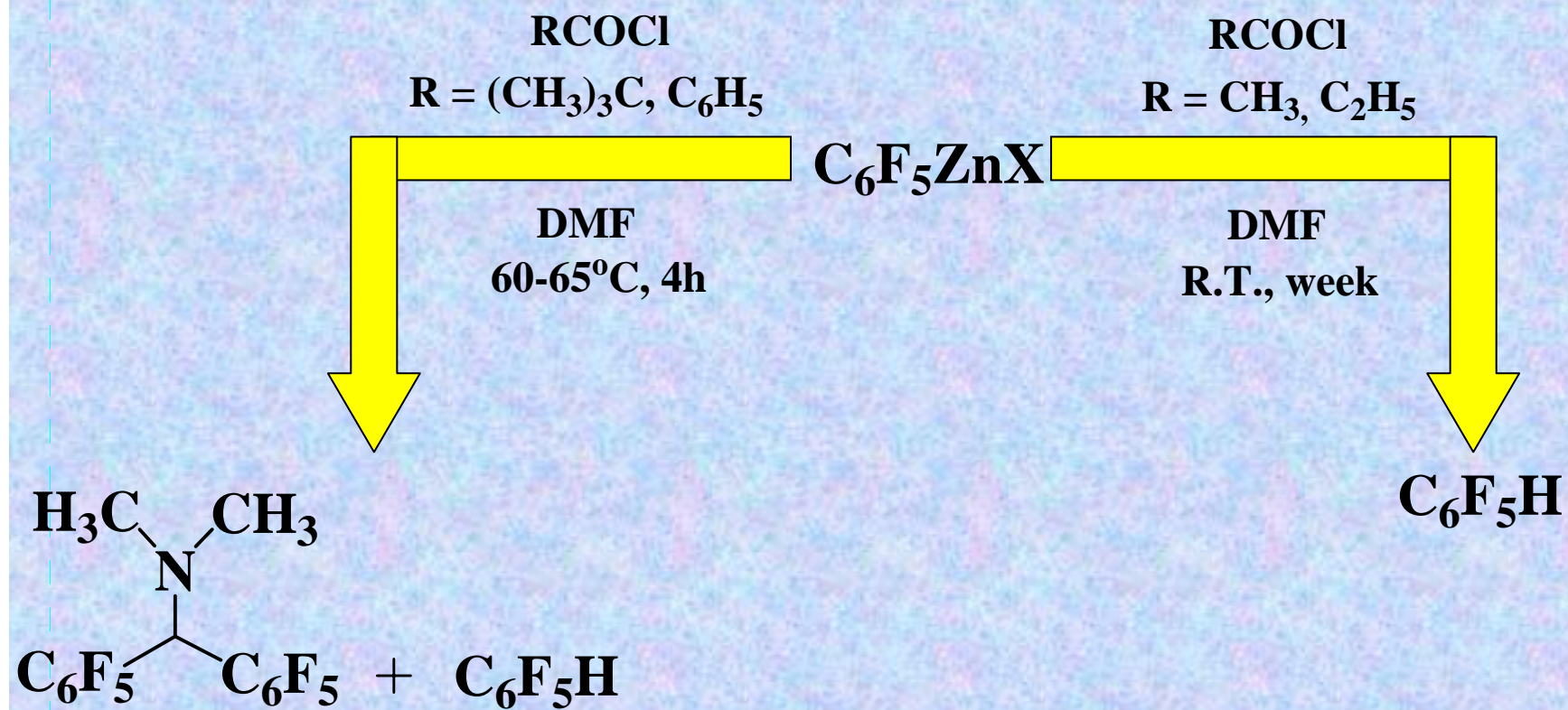


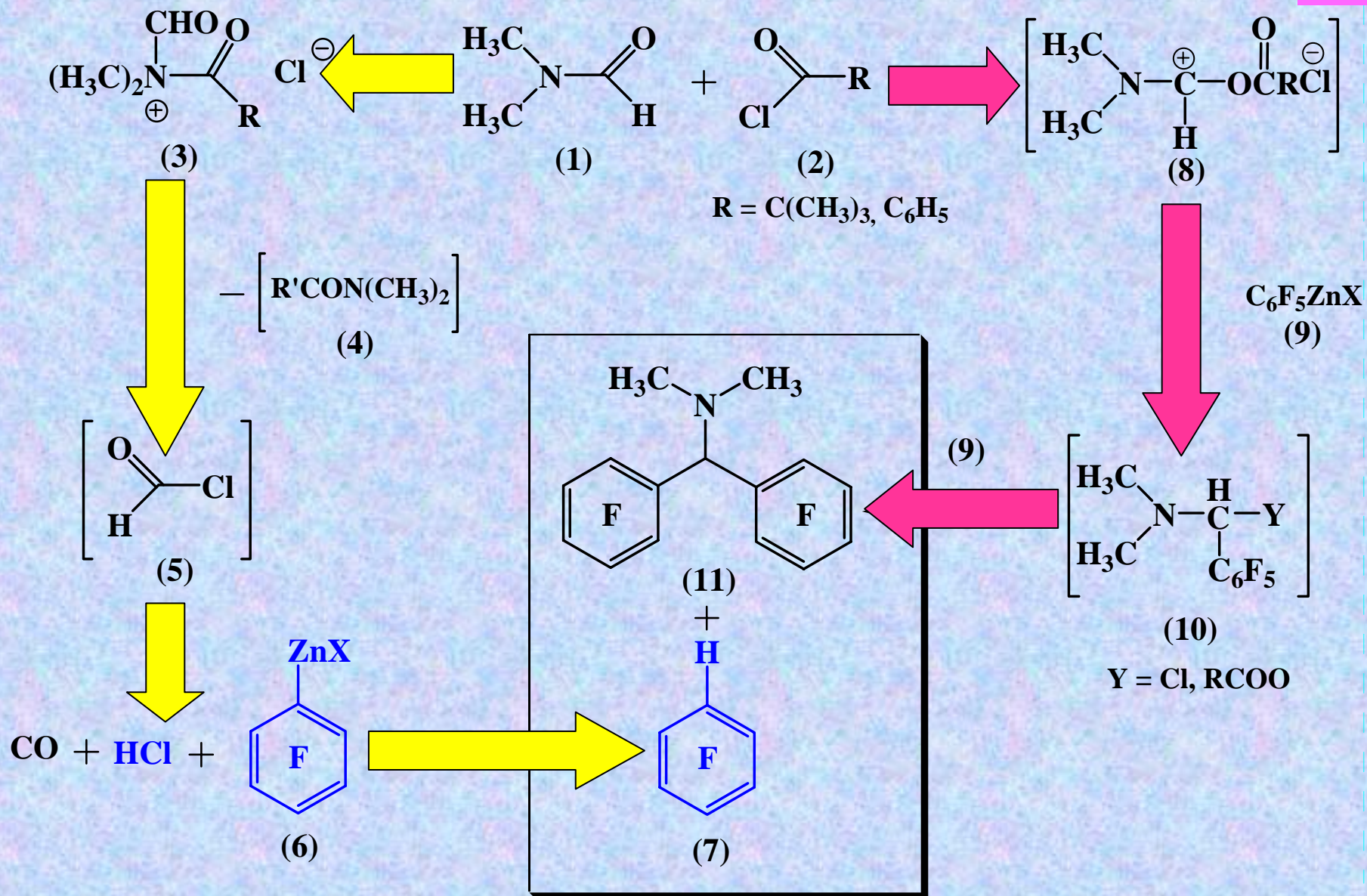


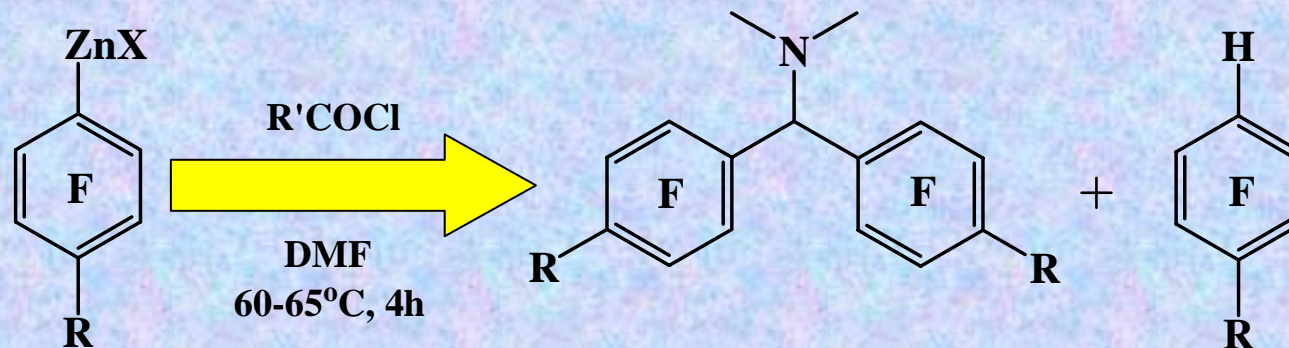


$\text{X} = \text{Cl}, \text{Ar}_f$









$\text{R} = \text{F}, \text{CN}, \text{CF}_3, \text{COOEt}$
 $\text{X} = \text{Ar}_f, \text{Cl}$

