

# Introduction to the Chemistry of Organosilicon Compounds

## Comparing silicon chemistry with carbon chemistry

CH<sub>4</sub> (methane)

SiH<sub>4</sub> (silane)

bp: -161°C

bp: -112°C

stable

in air

spontaneously

flammable

stable, insoluble

in water

rapid hydrolysis

(traces of alcali)



### Differencies:

- Electronegativity

C      Si      (H)

2.35    1.64    (2.79)

Si is more electropositive than C; e.g.



δ+    δ-

In general Si-X bond is more polar than C-X bond.

Some representative bond energies in  $\text{kJ mol}^{-1}$  (for homolytic fissions):

X:	C	Si	H	O-	N<
C-X	368	360	435	~360	~305
Si-X	360	340	393	452	322
X:	F	Cl	Br	I	
C-X	453	351	293	216	
Si-X	565	381	310	234	

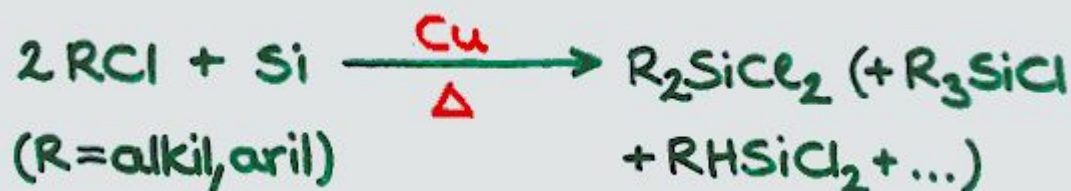
For instance,  $\text{Si}(\text{CH}_3)_4$  only starts to decompose above  $700^\circ\text{C}$ ;  $\text{Si}(\text{C}_6\text{H}_5)_4$  distillable at  $428^\circ\text{C}$  under atmosphere!

- Atomic radius of Si is bigger than C (covalent radii: 117 pm and 77 pm, respectively) • nucleophiles attack Si more easily
- Low energy empty *d* orbitals on Si • penta-/hexacoordination is possible

## Preparation of organosilicon compounds

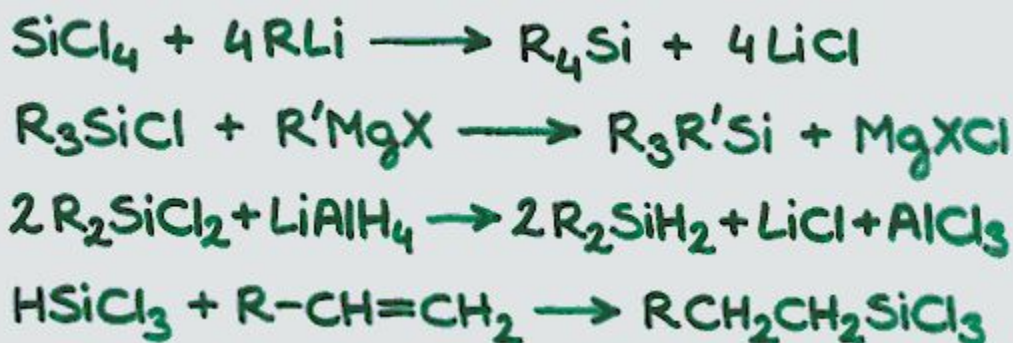
Chlorosilanes,  $\text{R}_n\text{SiCl}_{4-n}$  ( $n=1-3$ ), are of high account which are also important precursors themselves.

„Direct” synthesis (*Rochow-Müller*) used in industry:



Most important: R=Me (cf. silicones)

Methods mainly used in lab:



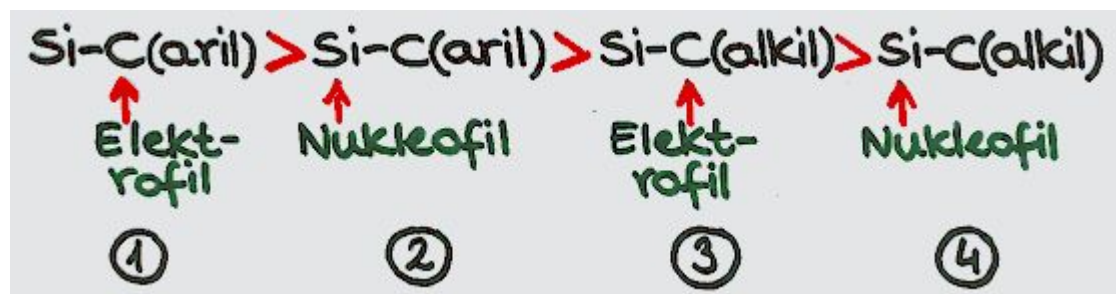
hydrosilylation (anti *Markovnikoff* regioselectivity)

## Reactions with Si-C bond fission

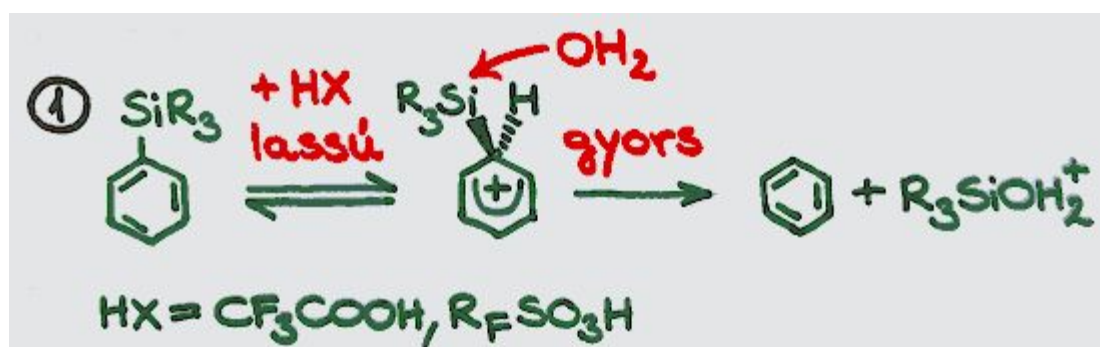
Not only the fissions of homolytic type do not undergo readily but also the heterolytic ones (low polarity of Si-C bond).

However, for instance, in  $\text{R}_3\text{SiR}'$  compounds there is a good correlation between the aptitude of the Si-C(R') bond breaking and the C-H acidity of the parent R'H compound ( $\text{R}_3\text{Si-C}\equiv\text{CR}$  desilylates easily)!

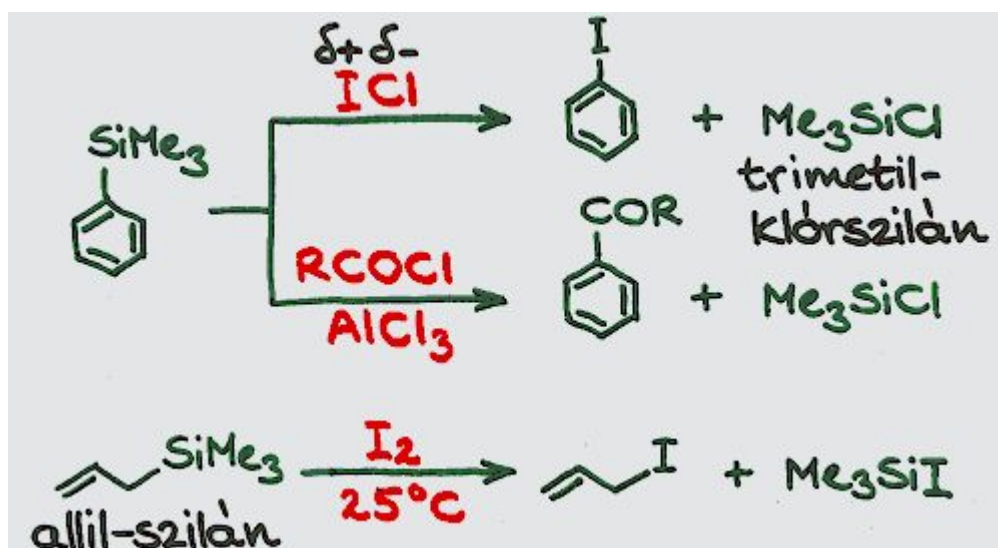
In general the order of the ease of Si-C bond fission:

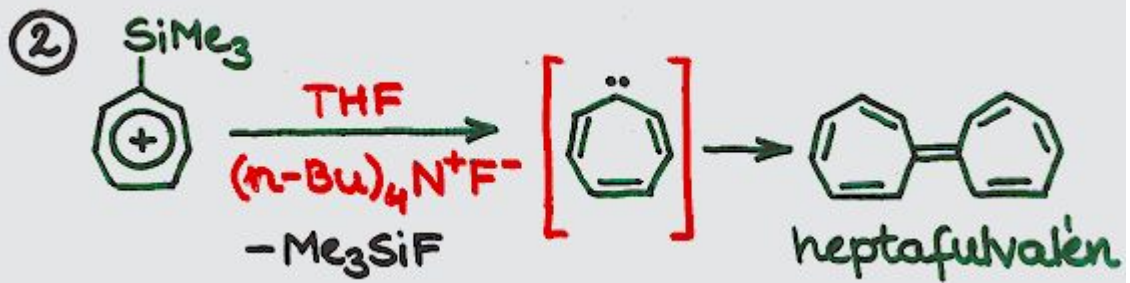


Examples:

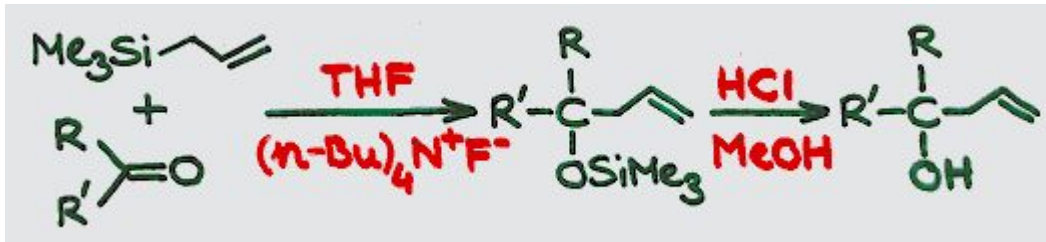


The rate of the R<sub>3</sub>Si→H exchange is 10<sup>4</sup> times higher than that of the H→H!

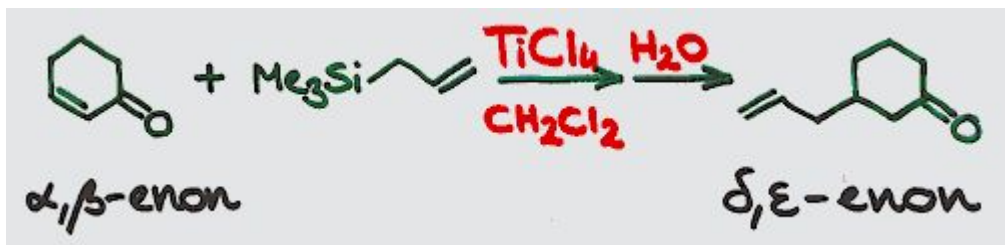




Sakurai reaction:



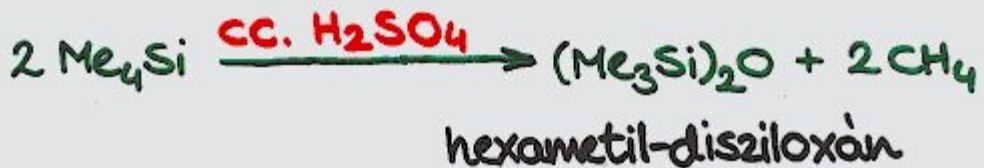
and its more frequently used version:



③ In the presence of strong Lewis acid catalyst:



Slow fission in the presence of cc. acid:



④

Only in the presence of very strong nucleophiles in aprotic medium:



But fissions can occur much more readily, for instance,

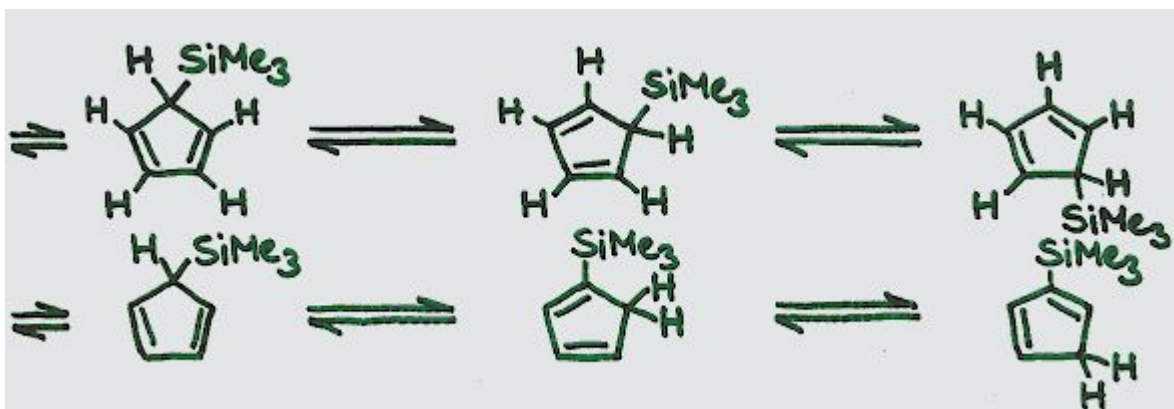
- if ring strain releases:



- if a good leaving group is found in  $\beta$  position:



In trimethylsilyl-cyclopentadiene the migration rate of the  $\text{Me}_3\text{Si}$  group is  $10^6$  times higher than that of the H atom:



# Reactions with Si-Heteroatom bond fission

In organosilicon compounds, due to the relative inertness of the Si-C bond, the Si-X bond is usually much more readily cleaved. (In a strict sense, such reactions should be discussed rather in the inorganic silicon chemistry.)

## Organosilanoles and silicones

Organo-chlorosilanes,  $R_nSiCl_{4-n}$ , rapidly hydrolyse to  $R_nSi(OH)_{4-n}$  which are condensating, e.g.:



driving force:  $E_{\text{Si-O}} > E_{\text{Si-Cl}}$  and  $\Delta_{\text{aq}} H(\text{H}^+, \text{Cl}^-)$

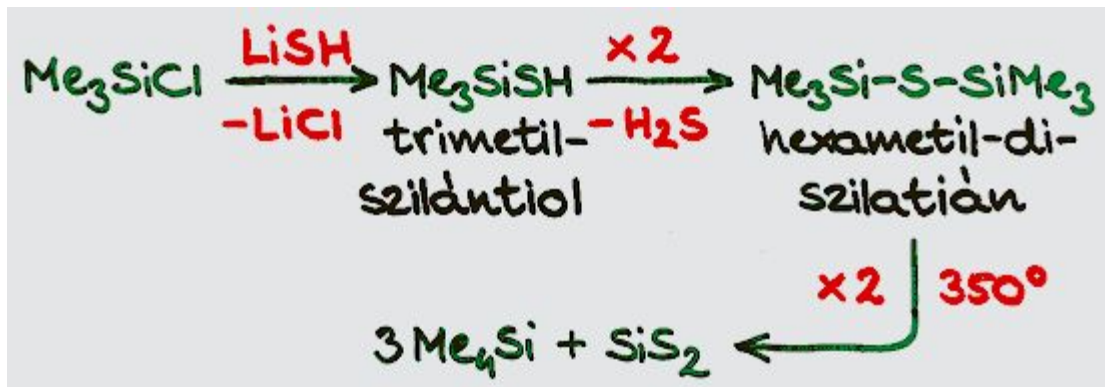
In the case of bifunctional chlorosilanes:



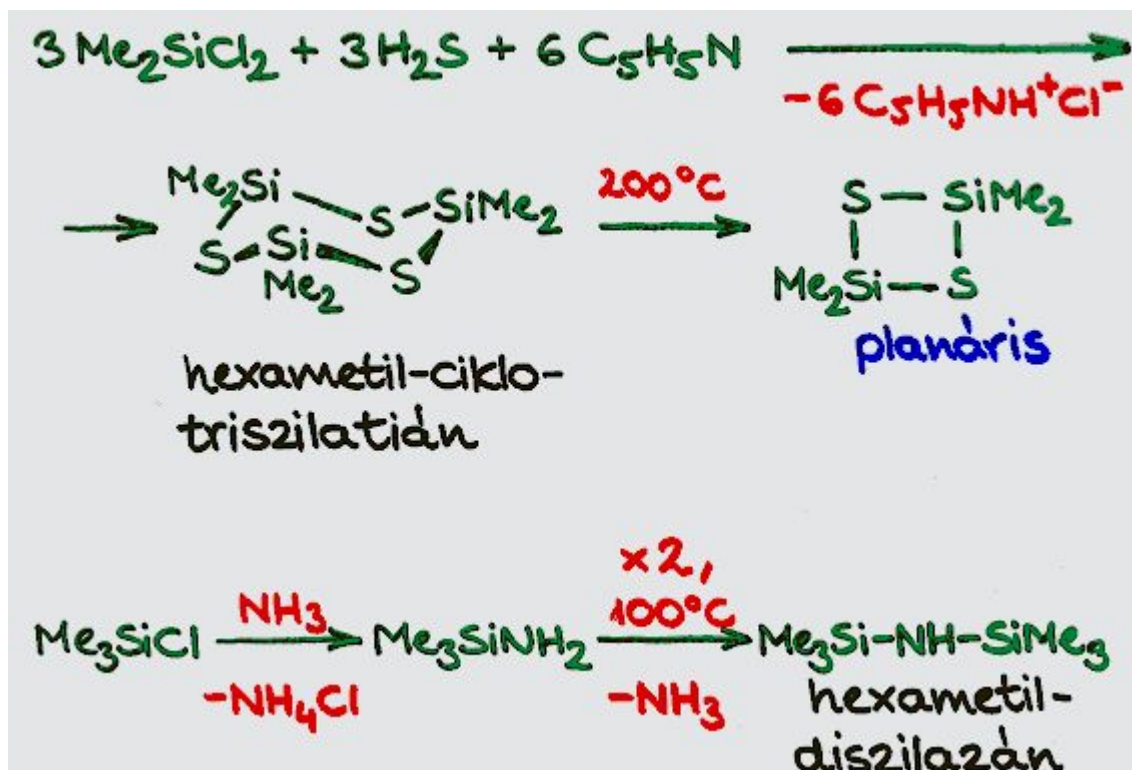
chains, rings

$(R_2\text{SiO})_n = \text{„poli-(sziliko-keton)}\text{“} = \text{szilikon}$

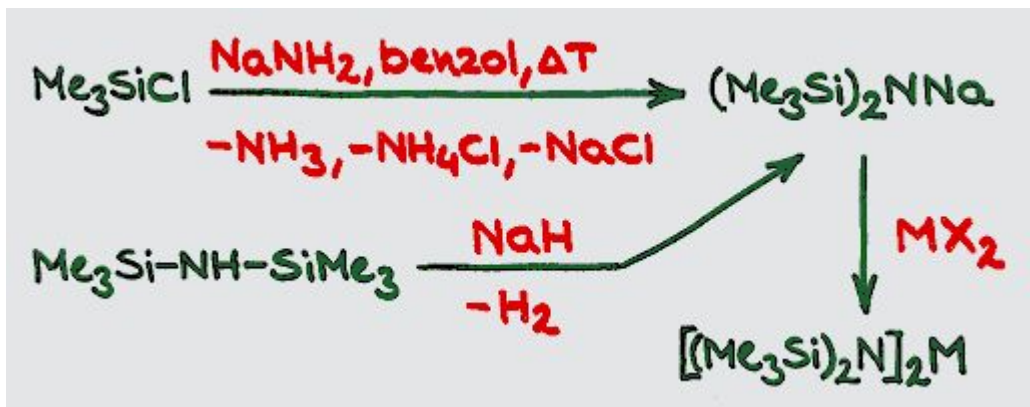
The chemistry of compounds containing  $R_3Si-E-$  or  $-R_2Si-E-$  ( $E=S,N$ ) unit



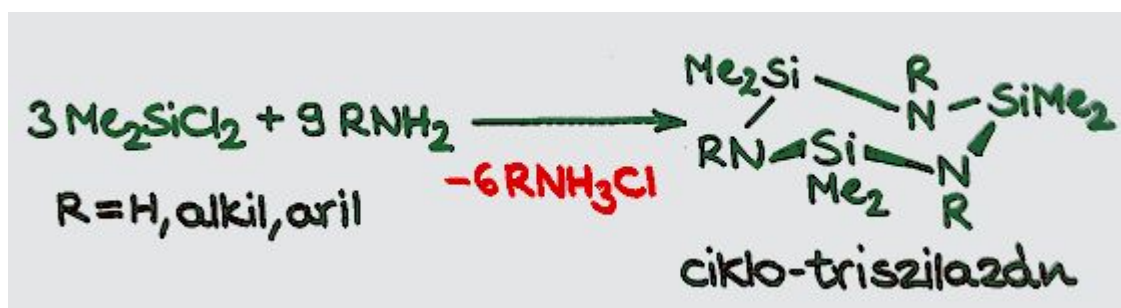
The Si-S bond is fairly stable thermodynamically, however, in contrast to the Si-O bond, it is moisture-sensitive.







e.g. M=Co; Metal complexes with low coordination number can be stabilized in this way!



It is difficult to prepare linear polyorganosilazanes,  $(-\text{R}_2\text{Si-NR}-)_n$  since mainly 6- (or 8-) membered rings form.

### Silylating agents

Silylation:  $\text{H} \rightarrow \text{SiR}_3$  (usually  $\text{SiMe}_3$ ) exchange.

Principally the silylation of organic compounds having mobile H atom (carboxylic acids, phenols, alcohols, thiols, amines, amides, carbohydrates, etc.) is of great importance.

## The silylation reaction:

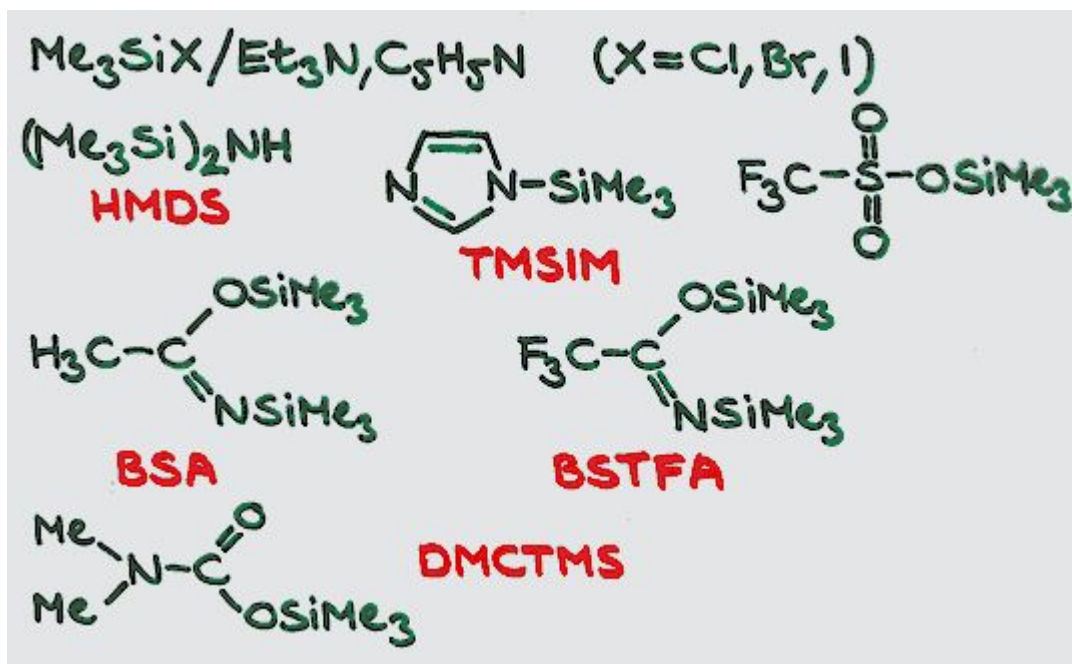


silylating agent

## The application fields of the silylation:

- enhancing volatility (GC, MS),
- attaching protective and/or activating group to organic compounds (chemical syntheses),
- hydrophobisation (silanisation), etc.

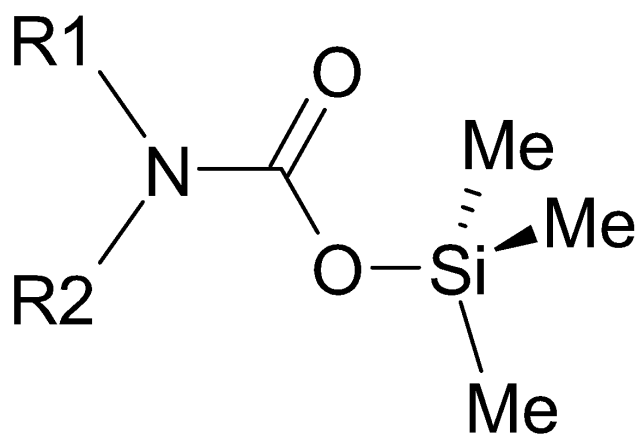
## More frequently used silylating agents:



Beside the  $\text{Me}_3\text{Si}$  group the following groups are also often used:  $\text{tBuMe}_2\text{Si}$ ,  $\text{Et}_3\text{Si}$ ,  $\text{iPr}_3\text{Si}$ ,  $\text{tHexMe}_2\text{Si}$ .

# Silylated carbamic acid esters

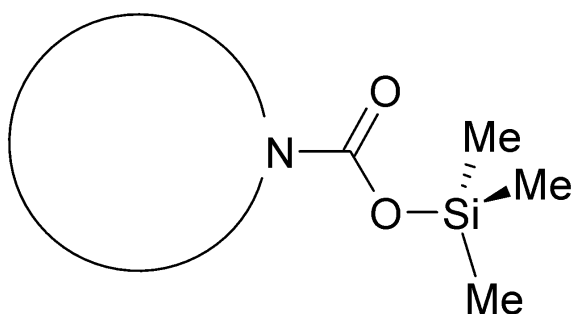
E.g.

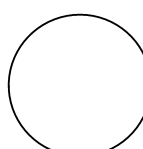


$R^1$  = alkyl, aryl, alkoxy

$R^2$  = H, alkyl, aryl,  $\text{SiMe}_3$

Aliphatic and aromatic N-heterocyclic derivatives:



 NH = pyrrole, indole, carbazole,  
pyrrolidine, indoline,

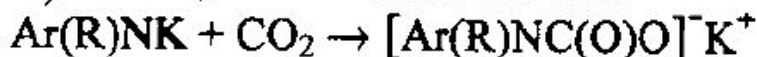
## Preparation of silylated carbamic acid derivatives

### 1.) Az amin karboxilezése:

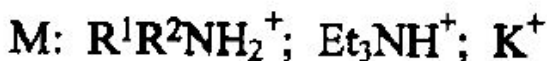
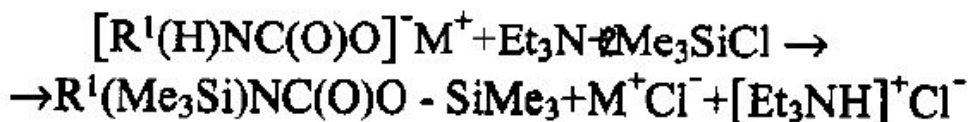
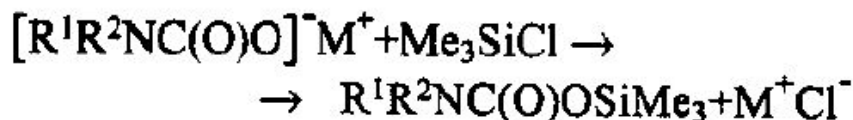
a.) alifás aminok:



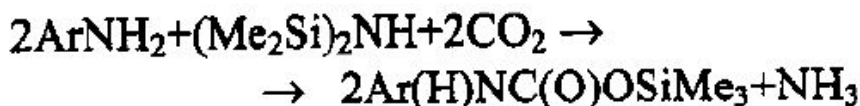
b.) aromás, heteroaromás aminok:



### 2.) Szililezés:



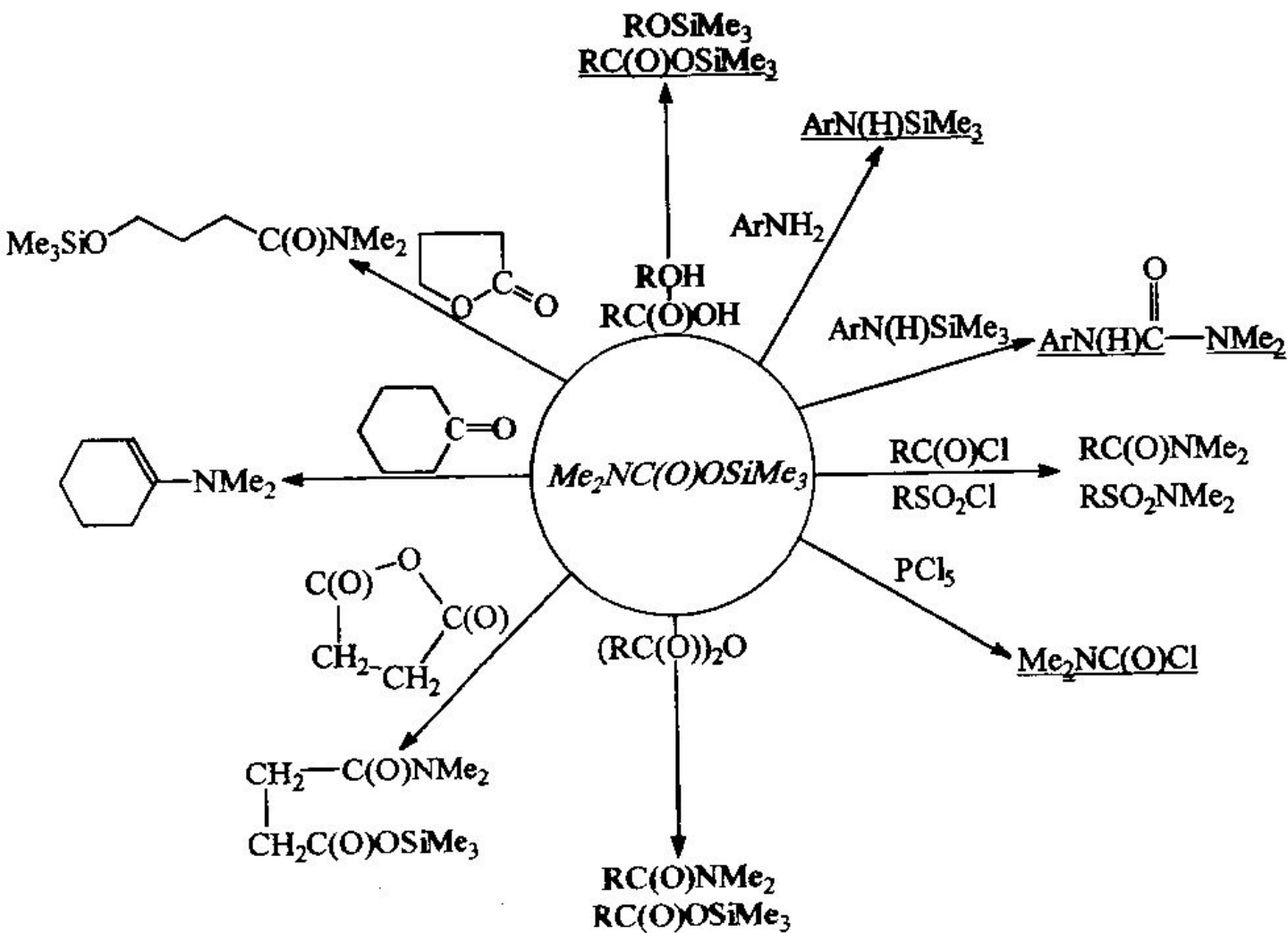
### 3.) Karboxiszililezés:



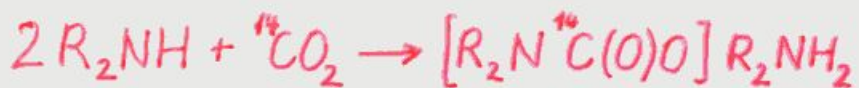
### 4.) Átszililezés:



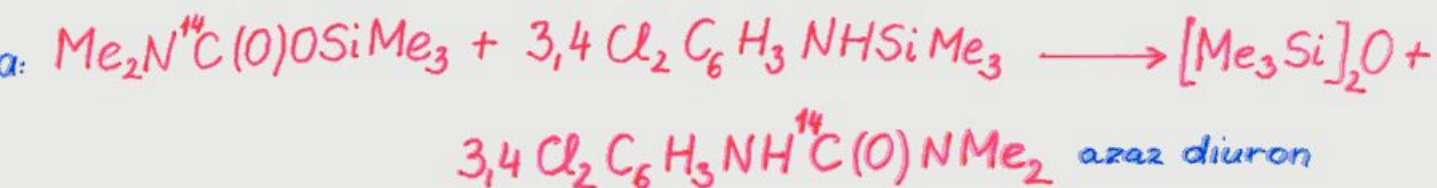
The reactions of DMCTMS  
(*N,N*-dimethyl-carbamic acid trimethylsilyl ester)



## Synthesis of herbicides with $^{14}\text{C}$ labelled carbonyl group



R: a = Me    b = n-Pr

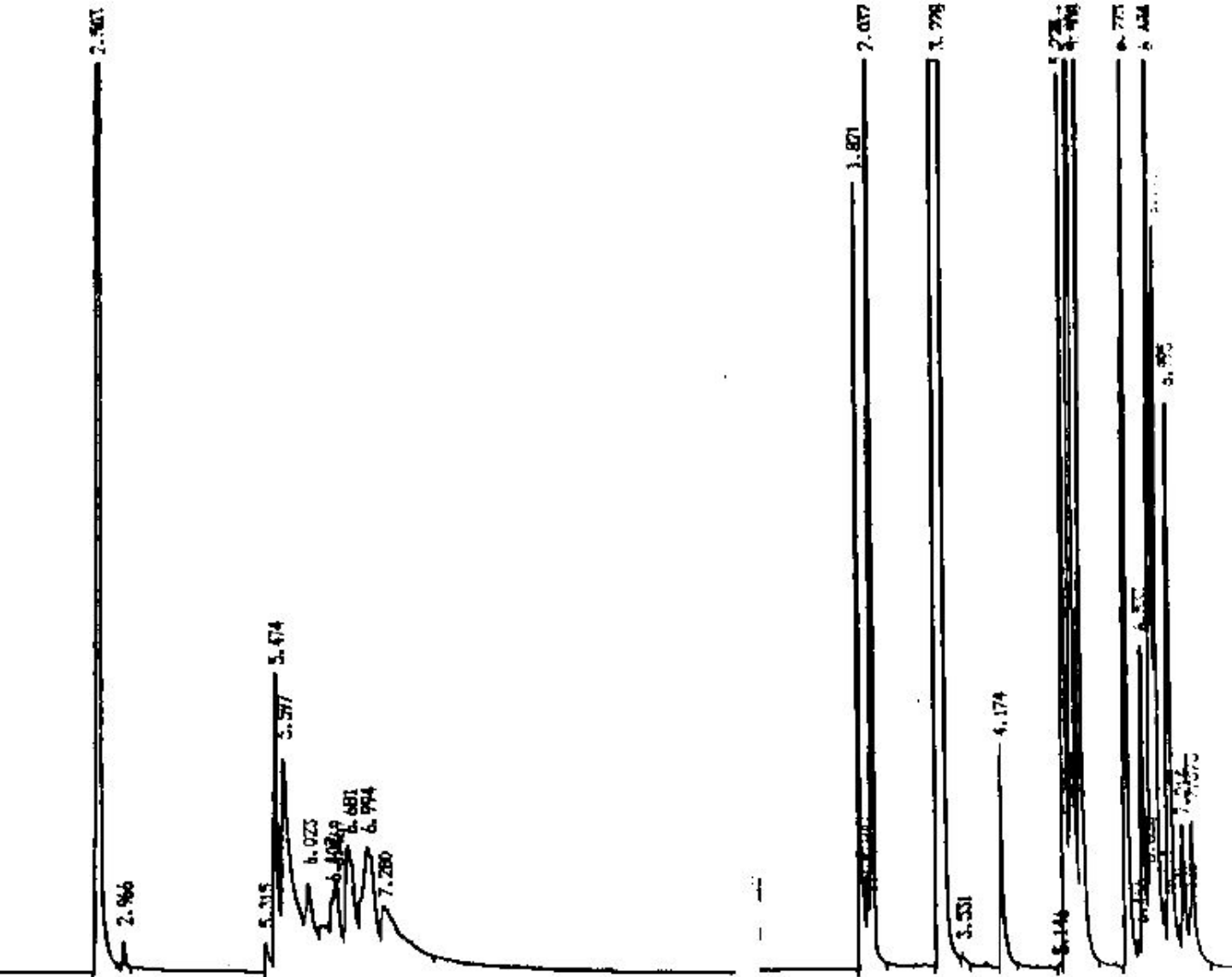


# The trimethylsilylation of phenols

## Gas chromatograms of

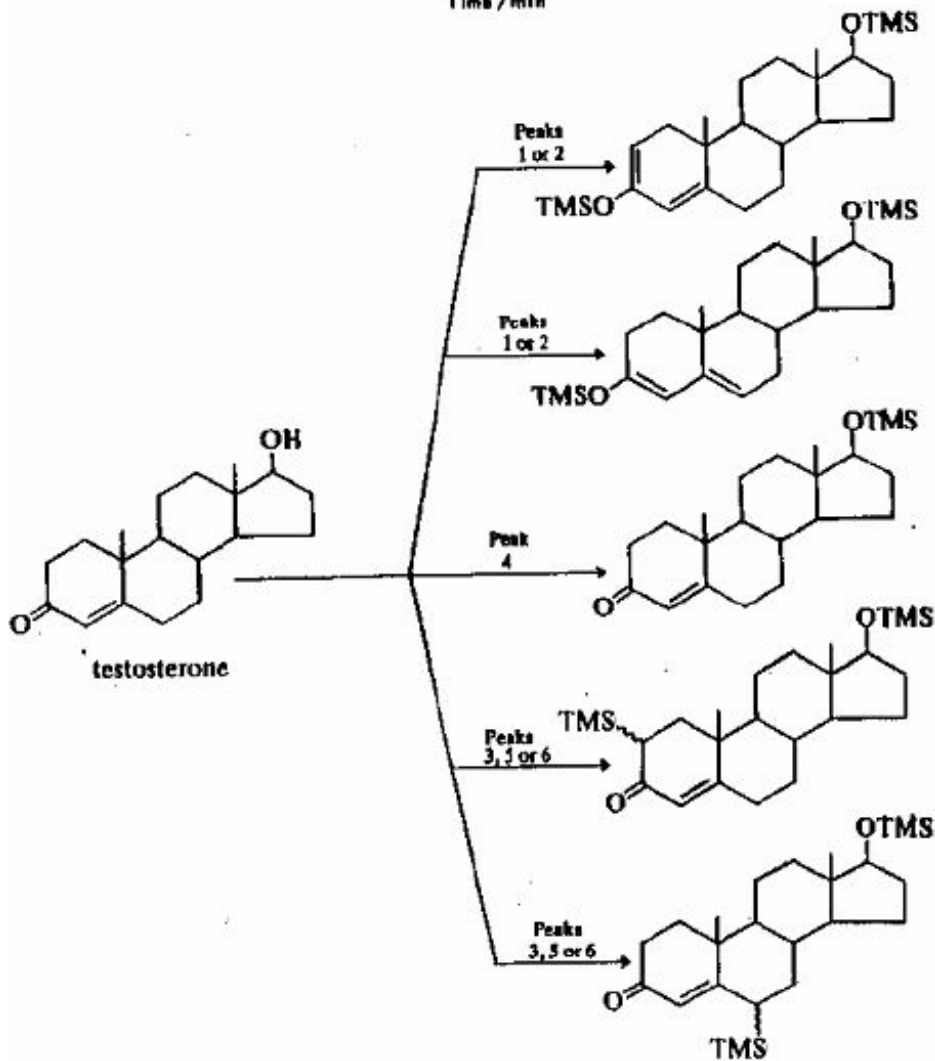
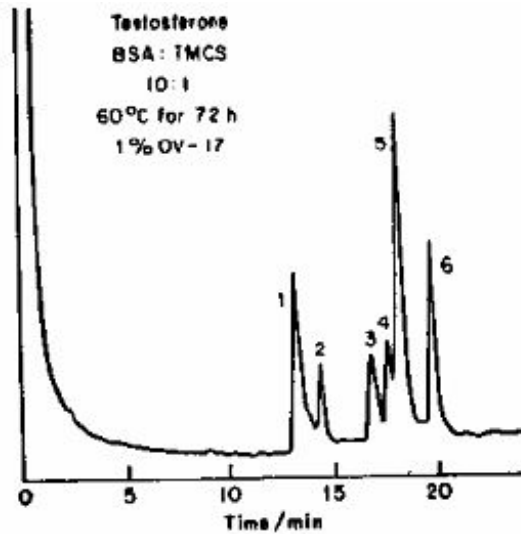
mixture of phenols

mixture of TMS phenols



# The silylation of steroids

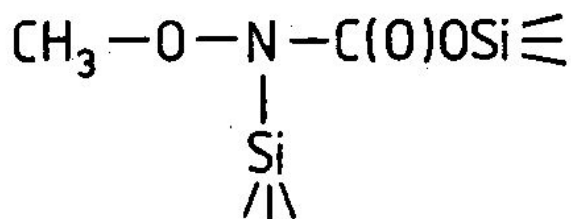
For example, the trimethylsilylation of the testosterone is not straightforward as six peaks appear on the chromatogram!





# The derivatization of testosterone

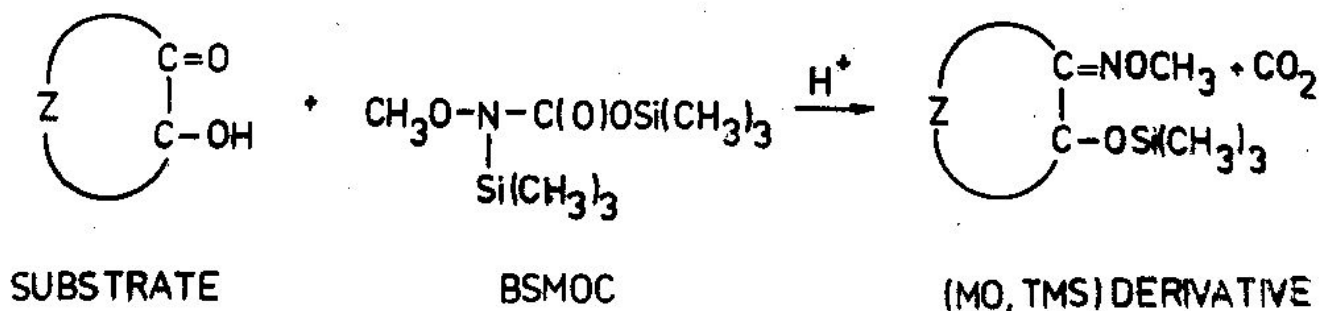
To solve the problem is the use of a derivatizing agent (BSMOC = *N,O*-bis-(trimethylsilyl)-*N*-methoxy-carbamate) capable of simultaneously silylating and methoximating the substrate!



BSMOC

RI: 1143 <sup>OV-1</sup>  
110°C

Bp: 55 - 58°C (2,5mbar)



**Scheme 1** Structure, characteristic GC-retention index and boiling point data of BSMOC reagent as well as schematic reaction with a hydroxy-keto substrate.

After 1 hour only one peak of the TMS+MO testosterone derivative is observable on the chromatogram!

TESZTOSZTERON-(MO, TMS)

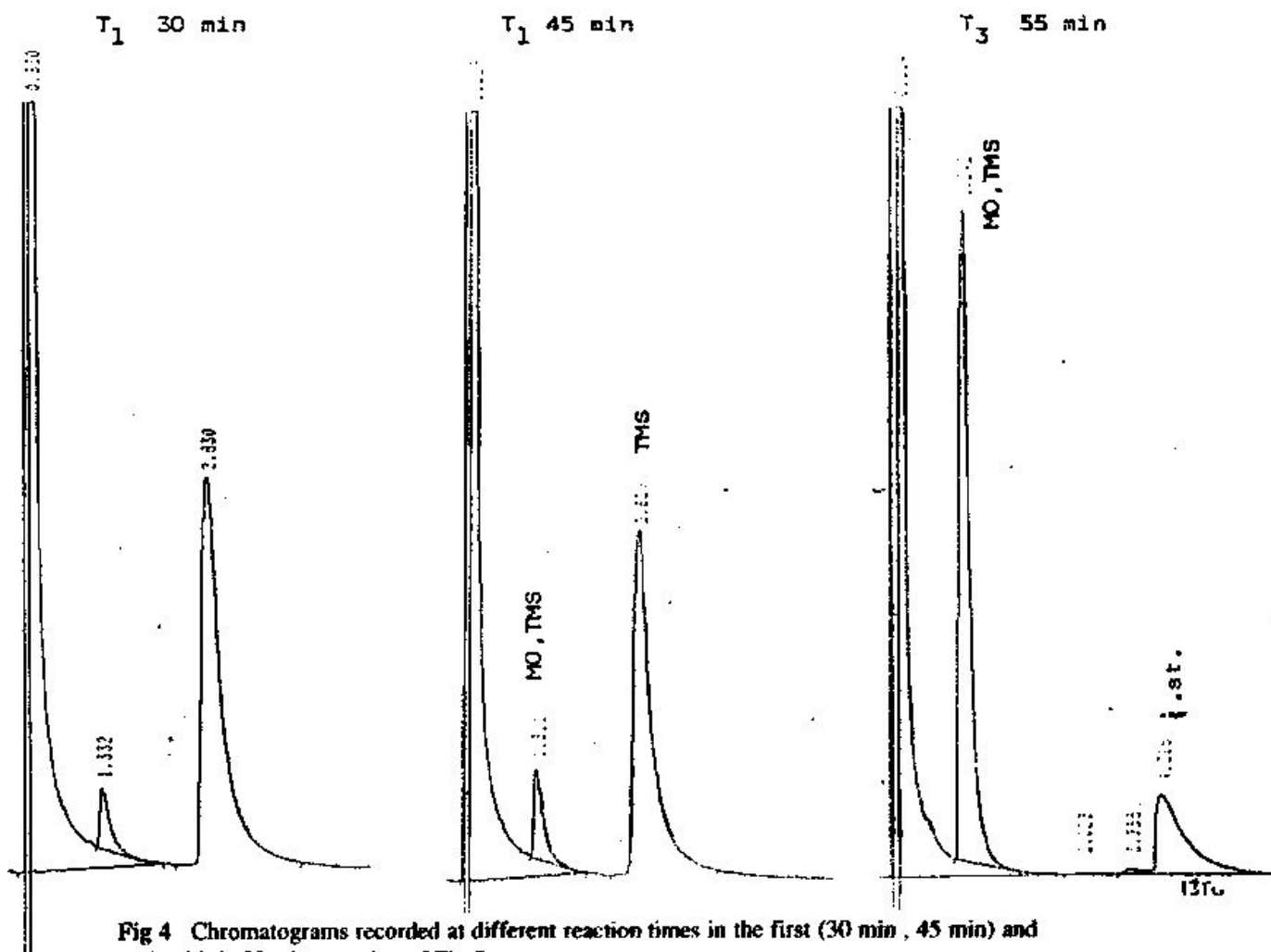


Fig 4 Chromatograms recorded at different reaction times in the first (30 min , 45 min) and in the third (55 min) reaction of Fig 3. (3% OV-210 column and 265°C thermostat temperature were applied).  
 Peaks : TMS - trimethylsilyl derivative of testosterone , MO,TMS - methoxime-trimethylsilyl derivative of testosterone, int.st. - cholesteryl acetate internal standard.