Теоретические основы органической химии

Кислородцентрированные соединения. Теория гибридизации.

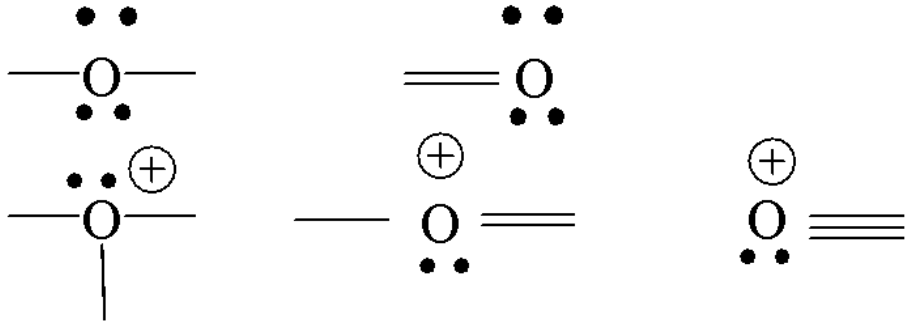
Лекция 6

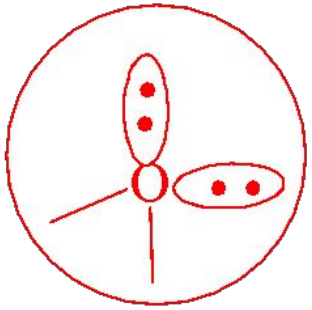
(электронно-лекционный курс)

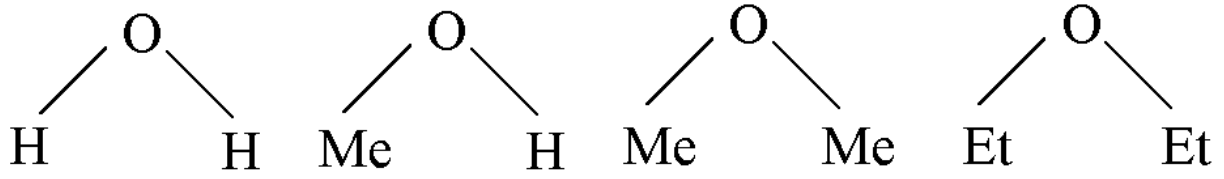
Проф. Бородкин Г.И.

Теория гибридизации (O)

O $1s^2 2s^2 2p^4$

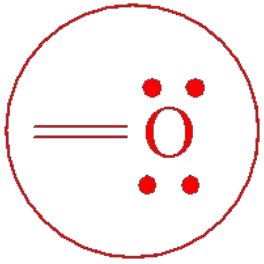


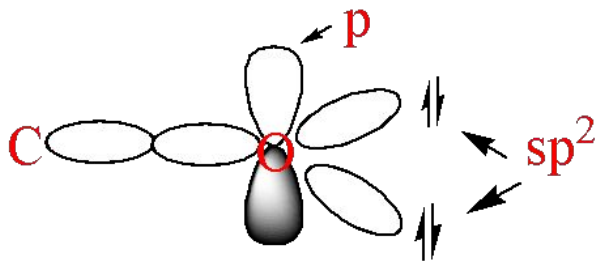


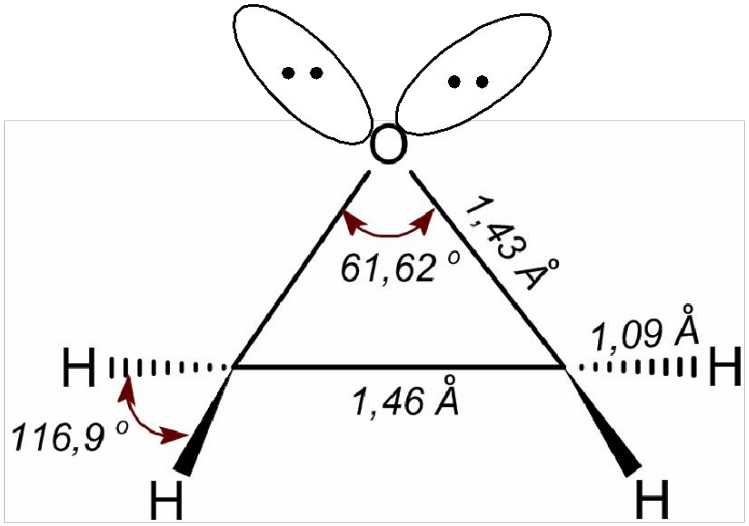


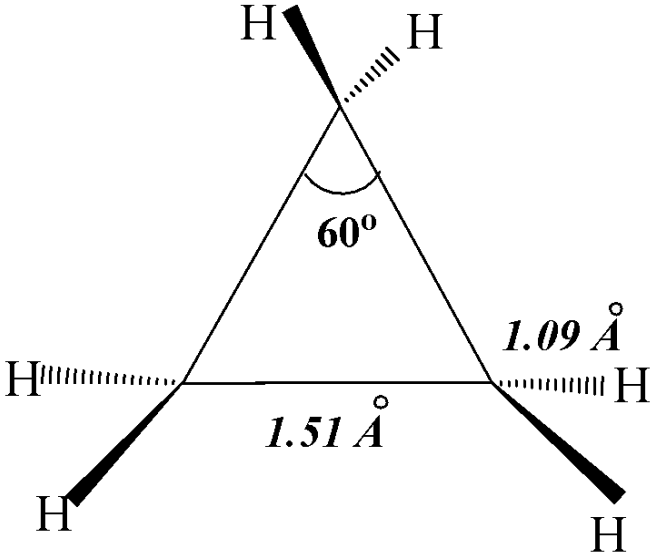
sp^3

∠ XNX 104° 105° 109° 108°









Энергия напряжения

25.1 ккал/моль

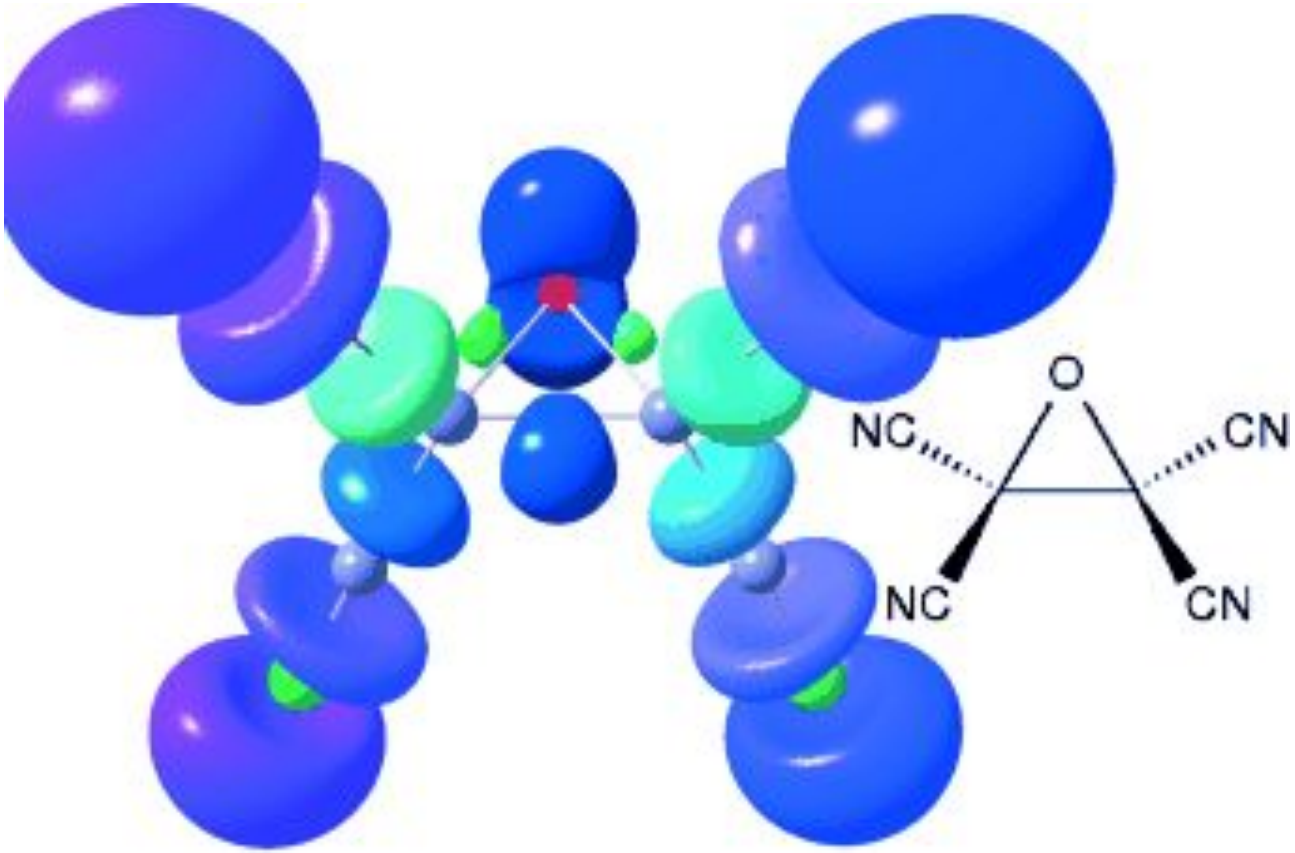
27.5 ккал/моль

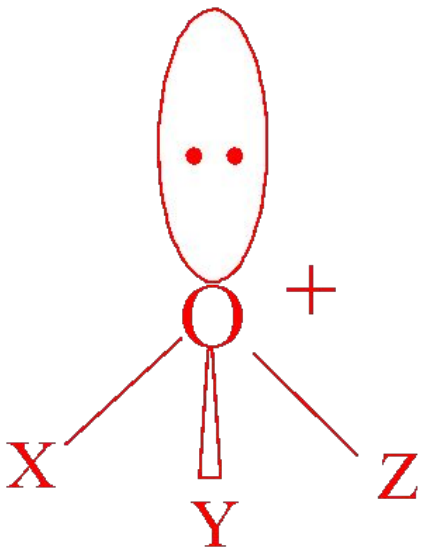
(при > 300 Cº)

$$(CH_2CH_2)O \rightarrow \bullet CH_2CH_2O\bullet \rightarrow CH_2O^{\cdot} + CH_2^{\cdot\cdot}$$

Распределение электронной плотности

(x-ray, 25k, ELI, электр. локализация неподел. пар)





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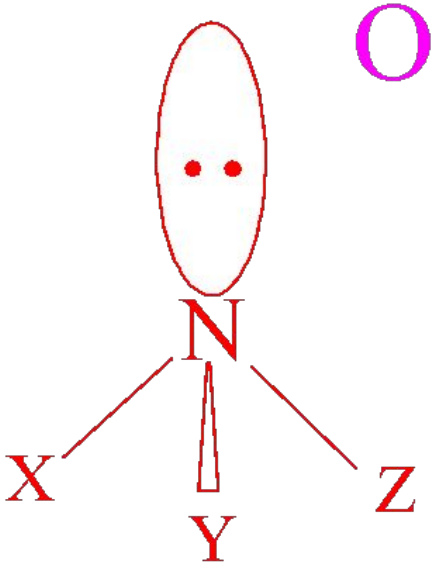
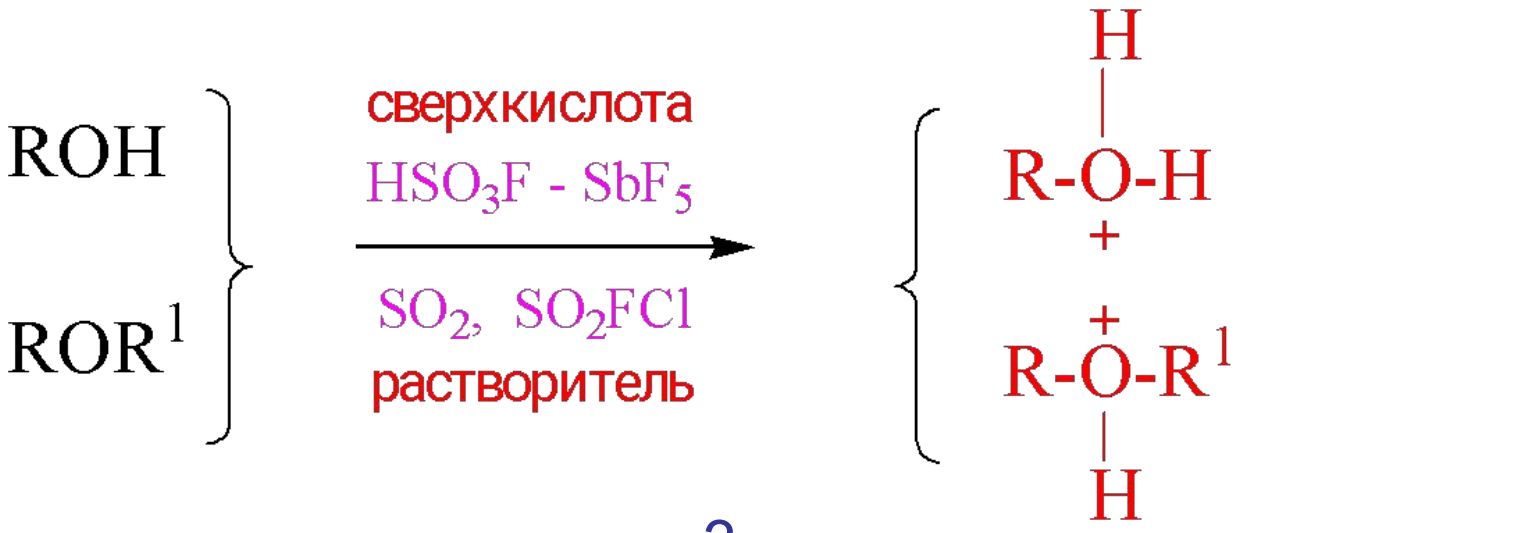


$O^+ \sim N$

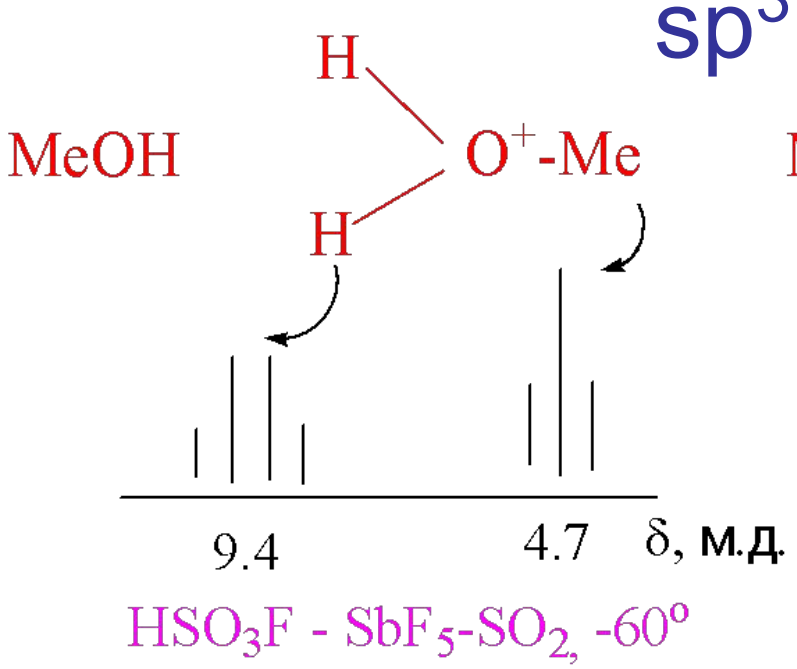
$\angle$ XOY = 105 - 110°

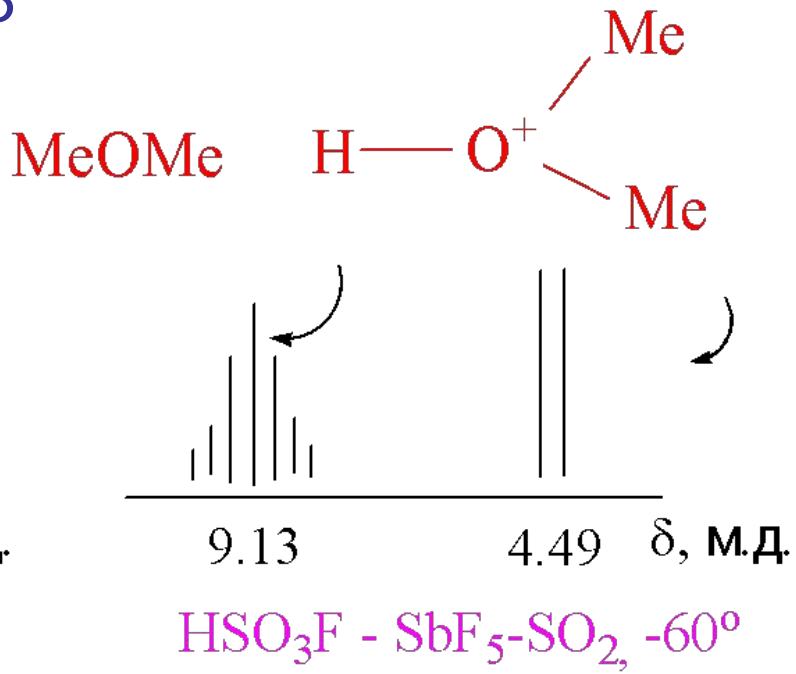
H_3O^+ по ИКС

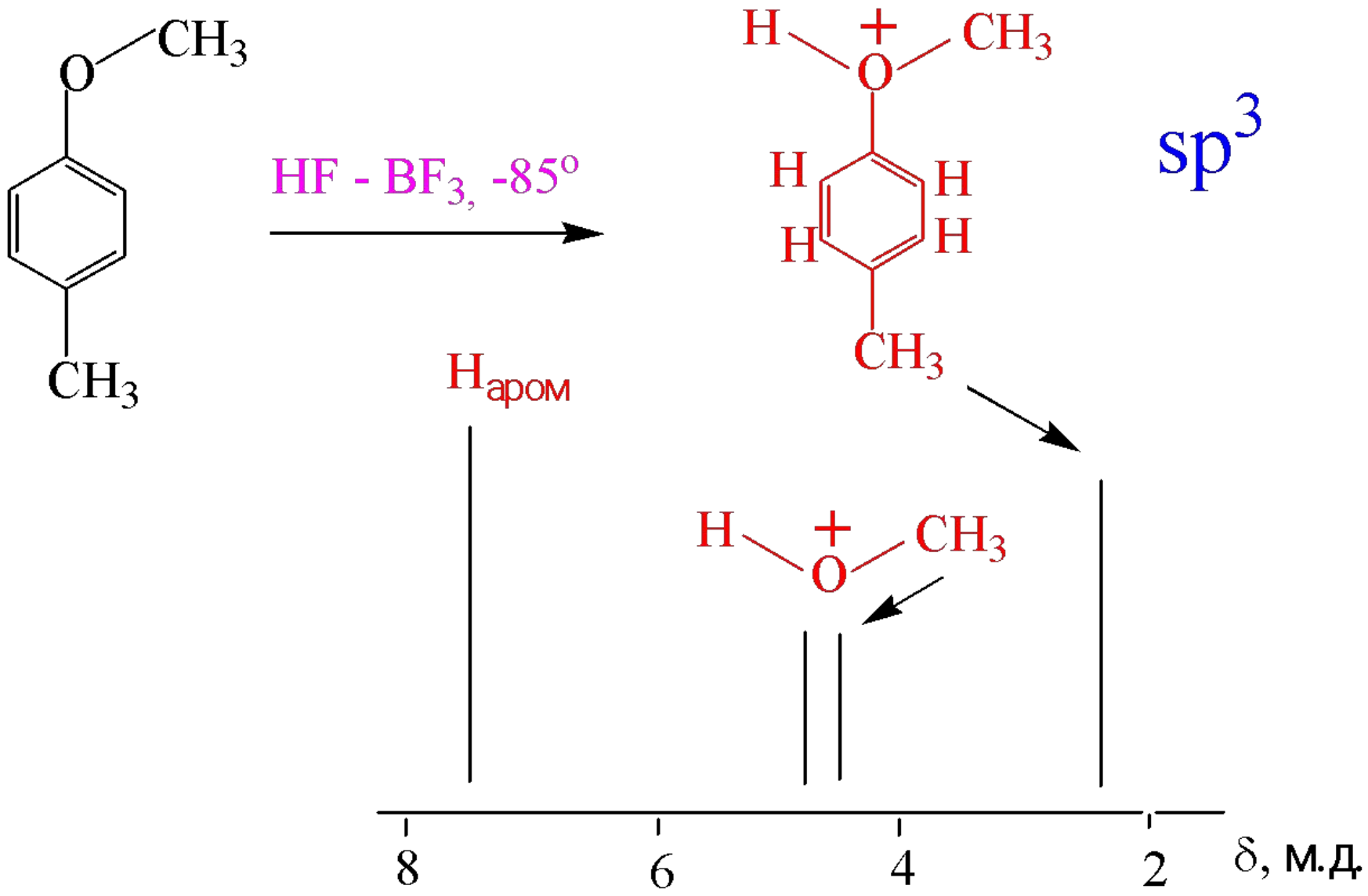
пирамида

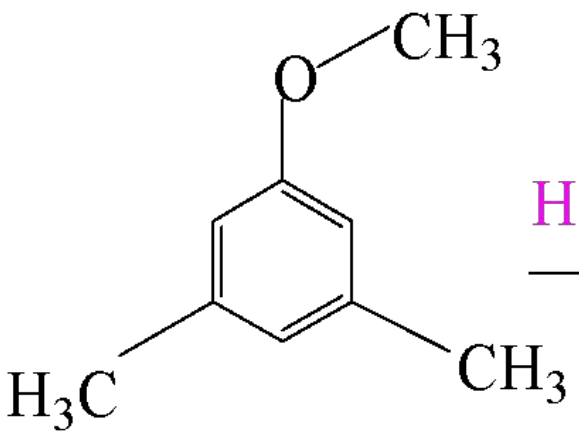

ROH
ROR1
сверхкислота
HSO3F - SbF5
SO2, SO2FCl
растворитель
H
R-O-H
+
+
R-O-R1
H

sp^3


MeOH
H
O+-Me
H
9.4
4.7
δ, м.д.
HSO3F - SbF5-SO2, -60°


MeOMe
Me
H
O+
Me
9.13
4.49
δ, м.д.
HSO3F - SbF5-SO2, -60°

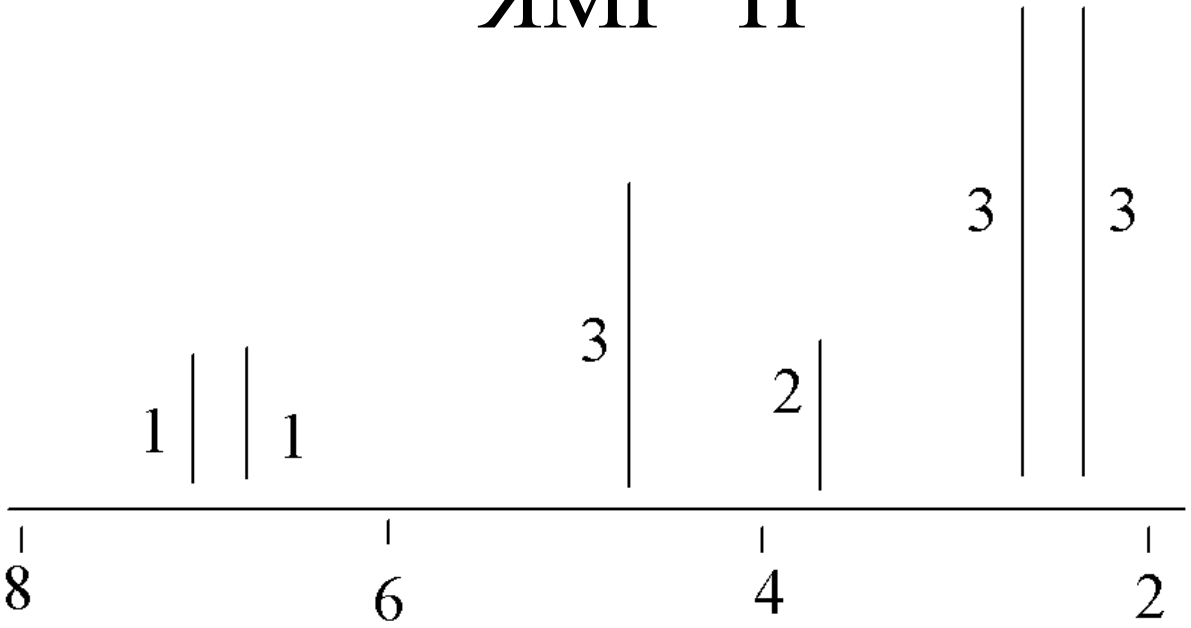

CH3
O
CH3
HF - BF3, -85°
H
+
O
CH3
H
H
H
H
CH3
sp3
Hаром
H
+
O
CH3
8
6
4
2
δ, м.д.

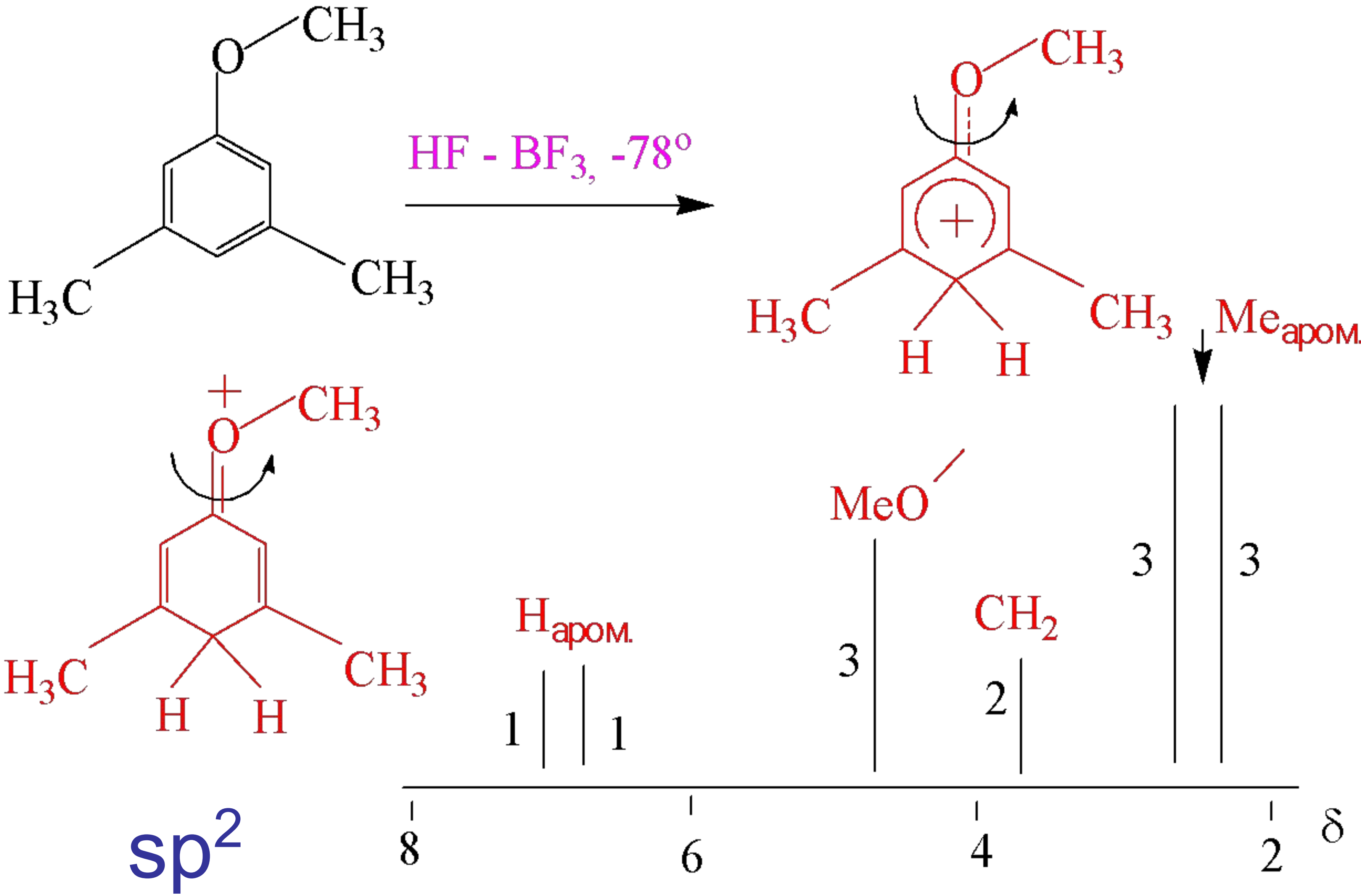


$HF - BF_3$, -78°

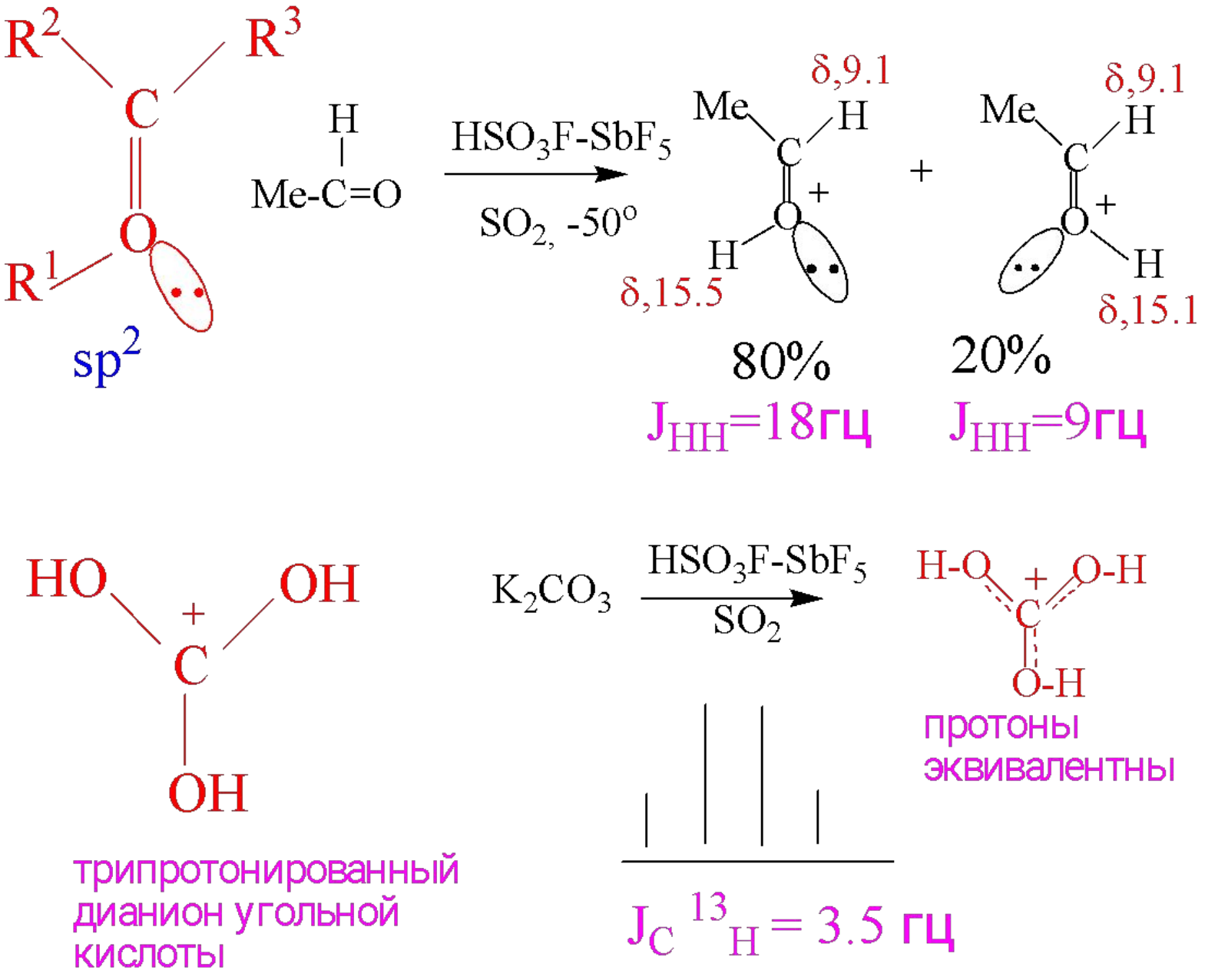
?

ЯМР ^1H

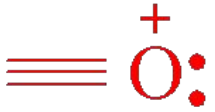




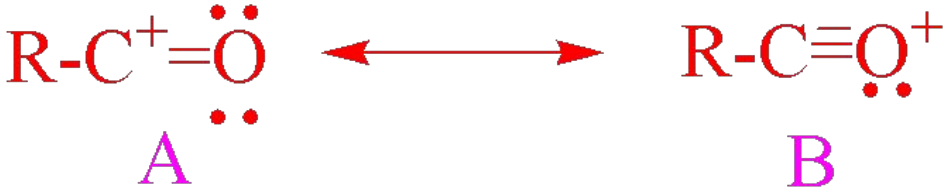
HF - BF3, -78°
Meаром.
MeO
Hаром.
CH2
1
1
3
2
3
3
8
6
4
2
δ
sp2


R2
R3
C
O
R1
sp2
H
Me-C=O
HSO3F-SbF5
SO2, -50°
δ,9.1
Me
H
C
+
O
H
δ,15.5
+
δ,9.1
Me
H
C
+
O
H
δ,15.1
80%
20%
JHH=18гц
JHH=9гц
HO
OH
+
C
OH
трипротонированный
дианион угольной
кислоты
K2CO3
HSO3F-SbF5
SO2
H-O
+
O-H
C
O-H
протоны
эквивалентны
JC 13H = 3.5 гц

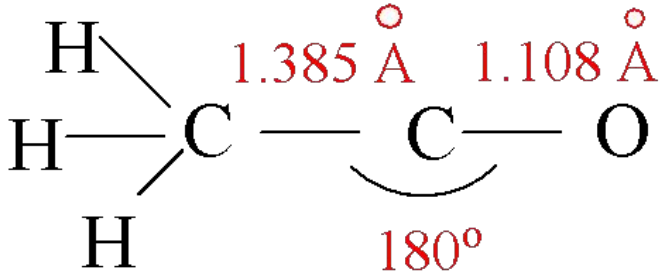
Соли ацилий-катионов

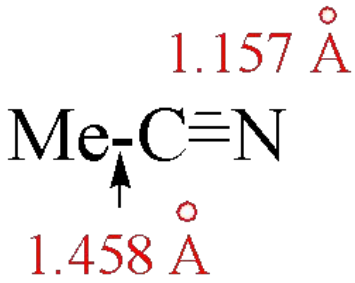


$$RCOCl + MeHal_n \longrightarrow RCO^+ + MeHal_{n+1}^-$$



РСА





ИКС

$\nu_{CO}^{+} = 2294$ см$^{-1}$ $\nu_{CN} \sim 2300$ см$^{-1}$

Галогениниевые ионы

$R\text{-}Hal^{+}\text{-}R$ J^{+} Br^{+} Cl^{+}

	J	Br	Cl	F
Ip, eV	10.5	11.8	13.0	17.4

$Ar\text{-}Hal^{+}\text{-}Ar$ (акад. Несмеянов)

$$PhN_2BF_4^- + PhBr \longrightarrow [PhBr^{+}Ph]\ BF_4^-$$

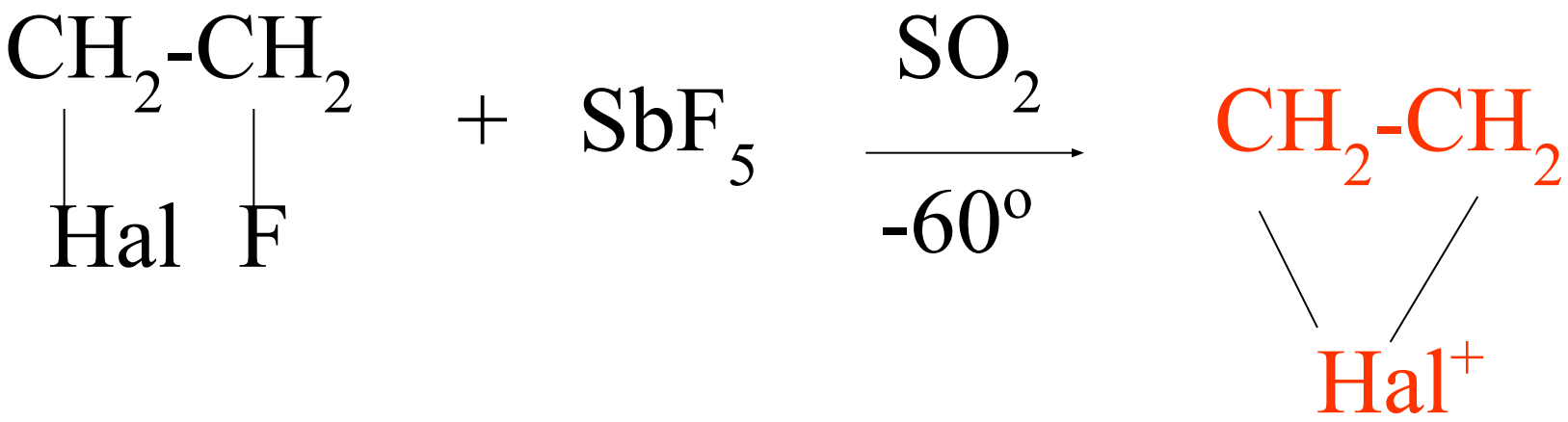
Т.пл. 120-121°

$$PhN_2BF_4^- + PhCl \longrightarrow [PhCl^{+}Ph]\ BF_4^-$$

Т.пл. 109-110°

Алкилгалогенониевые ионы

G. Olah, ЯМР

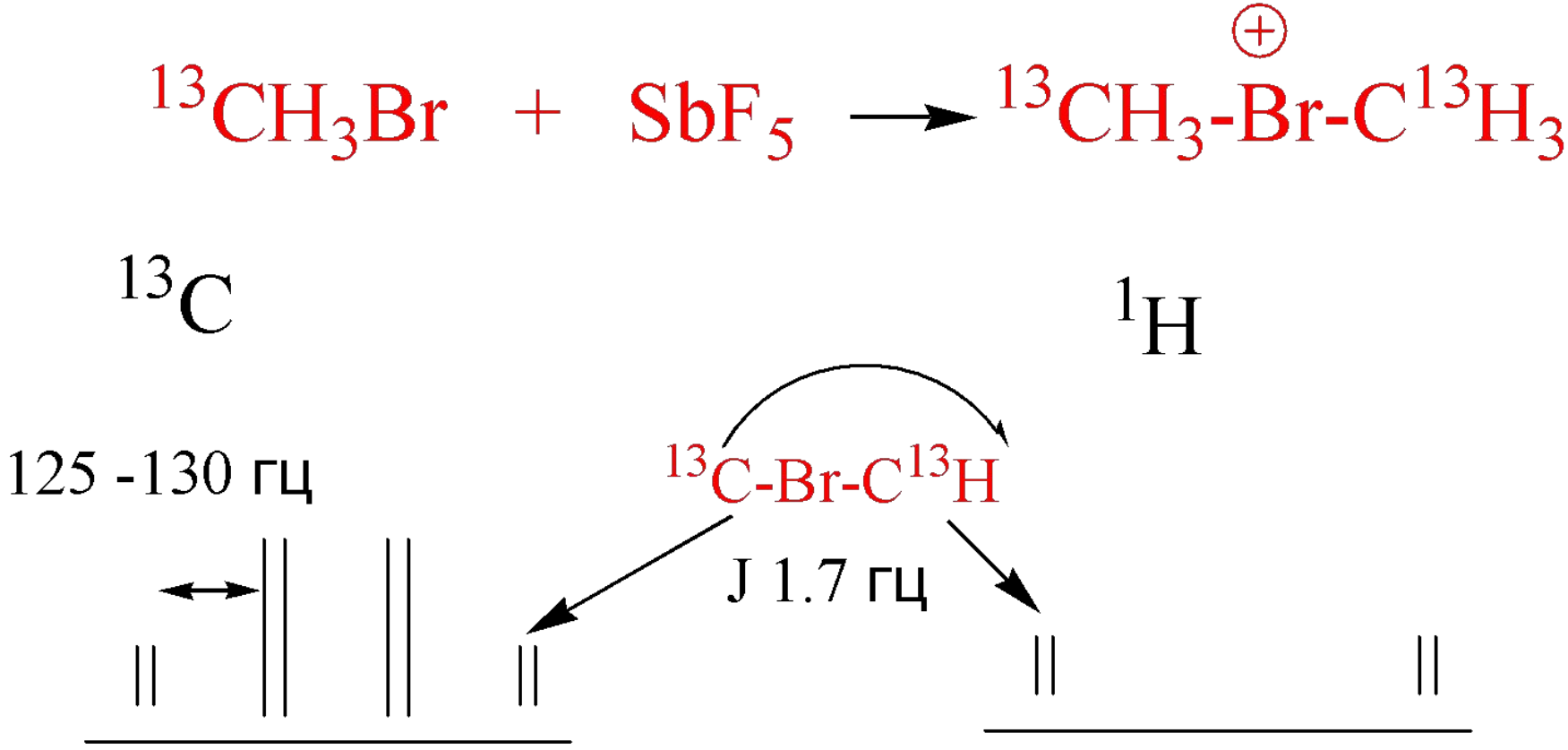


Hal = J, Br

$$2\ AlkHal + SbF_5 \xrightarrow[SO_2,\ -60^o]{SbF_5} [AlkHal^+Alk]\ SbF_5Hal^-$$

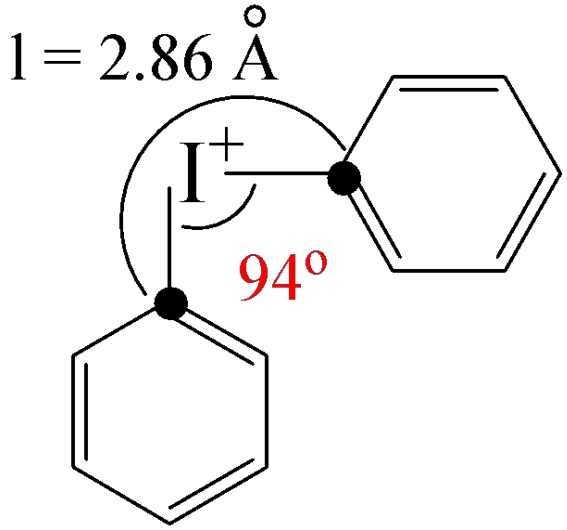
Hal = J, Br, Cl

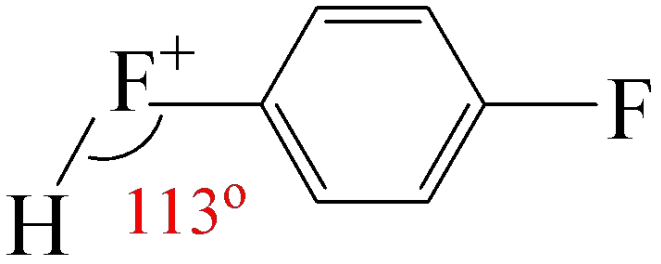
$AlkHal^+Alk$ или $AlkHal \rightarrow SbF_5^-$?


$^{13}CH_3Br + SbF_5 \rightarrow {}^{13}CH_3\text{-}\overset{\oplus}{Br}\text{-}C^{13}H_3$
^{13}C
^{1}H
125 -130 гц
$^{13}C\text{-}Br\text{-}C^{13}H$
J 1.7 гц

3-ий и более периоды ?

2-ой период	NH_3	OH_2
	107^o	104^o
3-ий период	PH_3	SH_2
	94^o	92^o
4-ый период	AsH_3	SeH_2
	91^o	90^o





B3LYP/6-311(2df,2pd)

Dopler et al., JACS **2003**,1421

$r_w^C + r_w^C = 3.0$ Å

Нет склонности к инверсии (P, As, Sb)

$\Delta G^{\neq}$ ккал/моль (ab initio)

NH_3	6	H_3O	1-2
PH_3	36	H_3S^+	32
AsH_3	46	H_3Se^+	30

Оптические антиподы

Alk^1-P-Alk^2

|

Ar

Alk^1-As-Alk^2

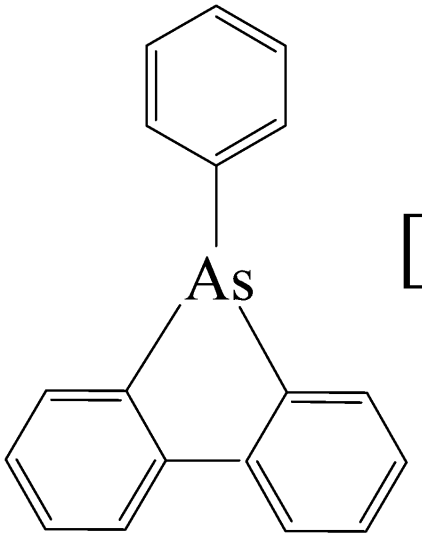
|

Ar

Alk^1-Sb-Alk^2

|

Ar



[α] +255°

не рацемизуется
при 110°

R^1-S^+-R^2

|

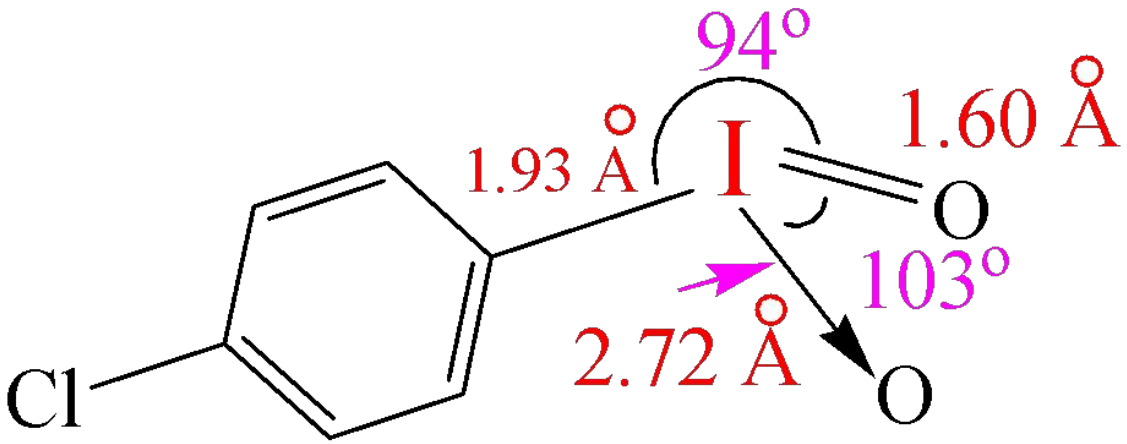
R^3

R^1-S^+-R^2

|

O^-

Katritzry et al.



Псевдооктаэдр.

от-но I, промеж.

AX_3E, AX_3E_2