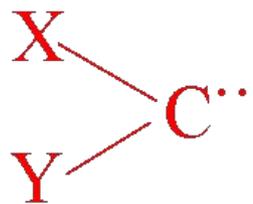


Теоретические основы органической ХИМИИ

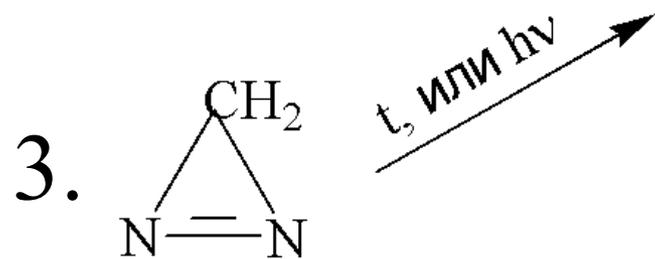
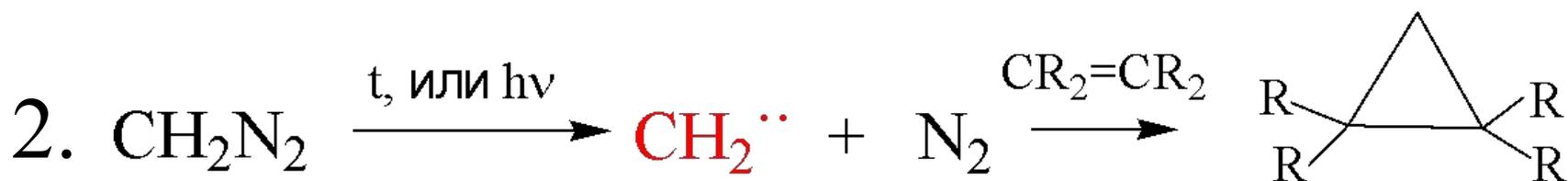
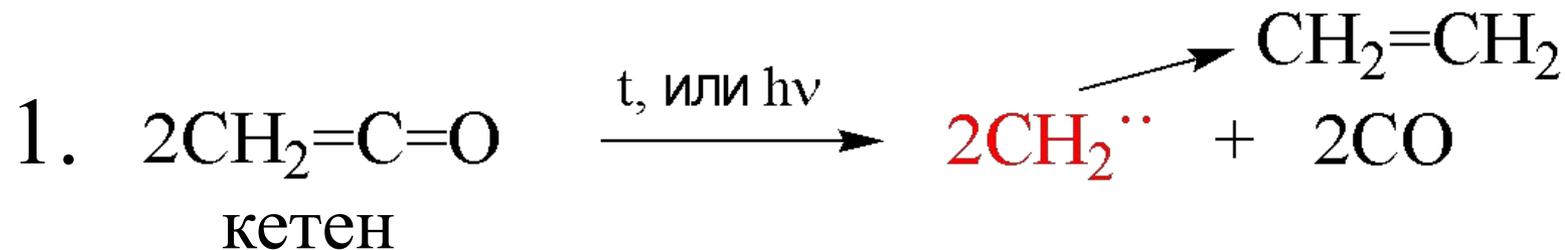
Карбены и арины. Строение и свойства.

Лекция 26
(электронно-лекционный курс)

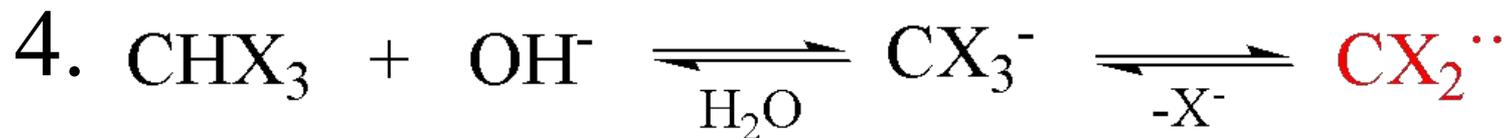
Проф. Бородкин Г.И.



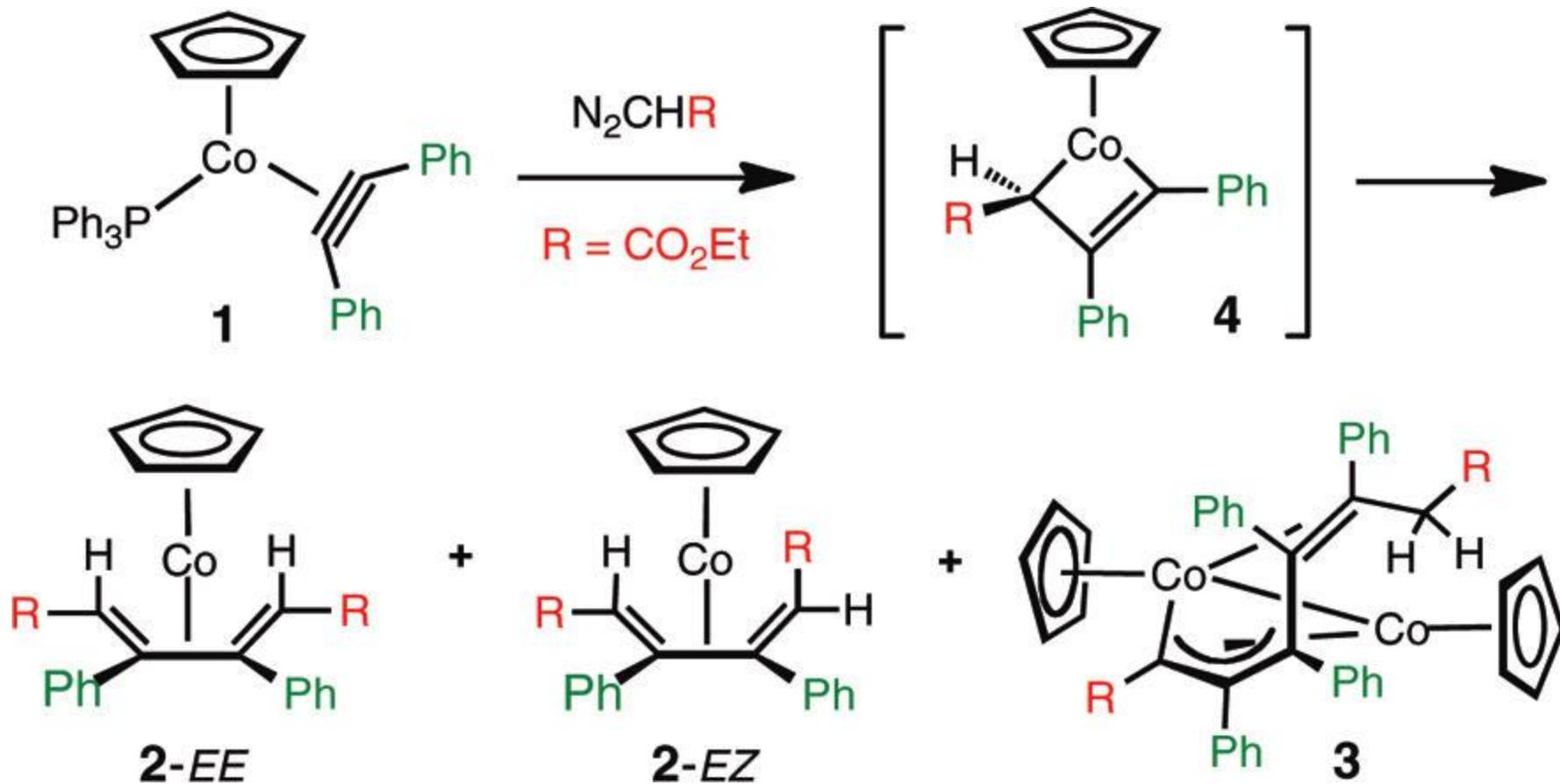
Карбены



диазирин



Реакции карбенов

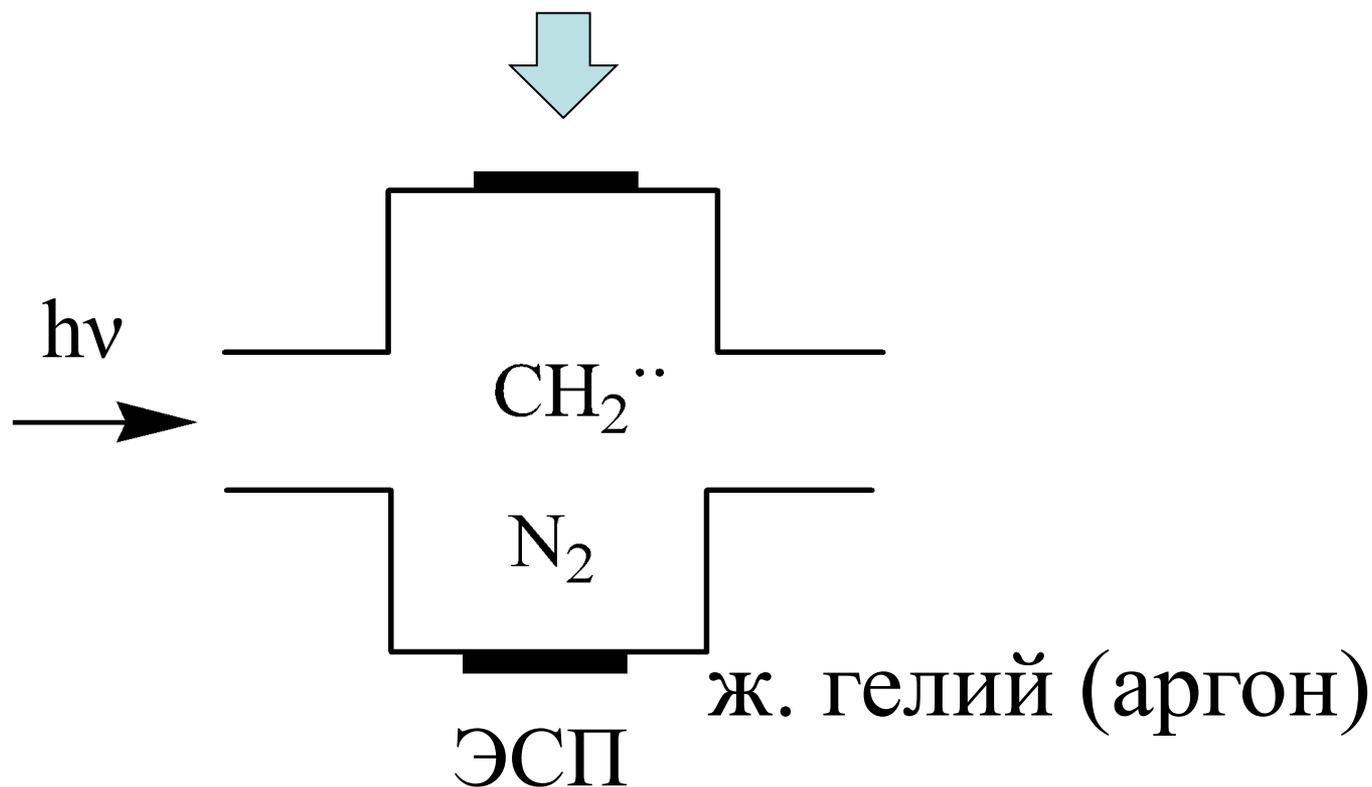


Методы изучения

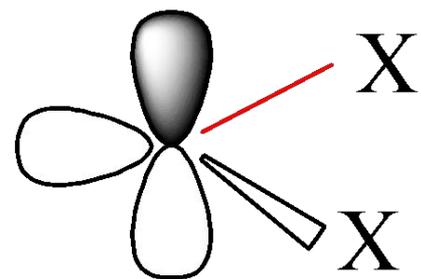
1. Импульсный фотолиз

Воздействуют светом и записывают ЭСП или ИКС за 10^{-5} с

2. Метод матричной изоляции

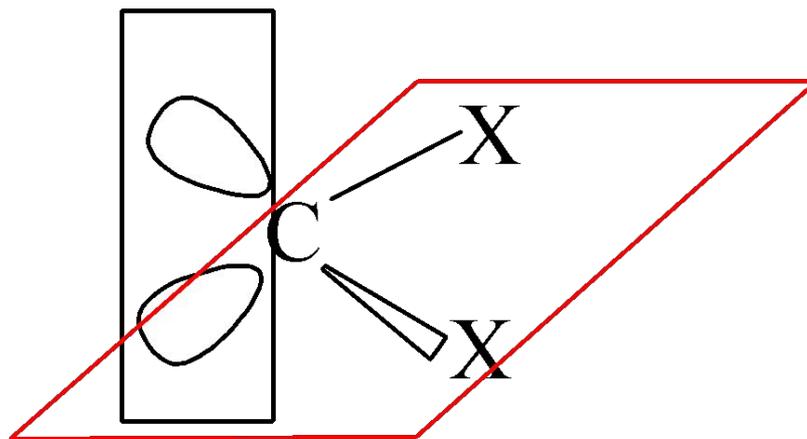


3. ХПЯ (хим. поляризация ядер)

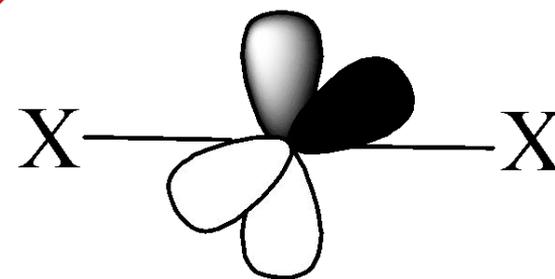


I
 sp^2 (S)

угловая модель



II
 sp^3 (T)

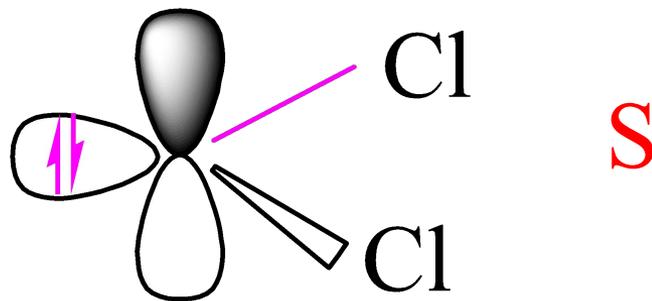
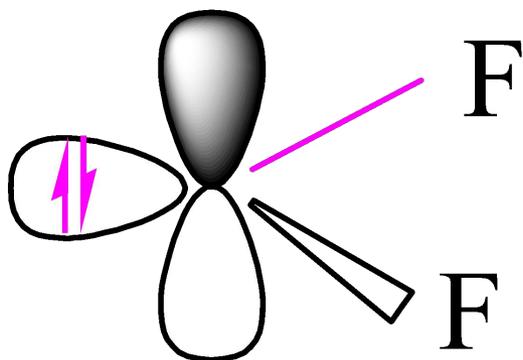
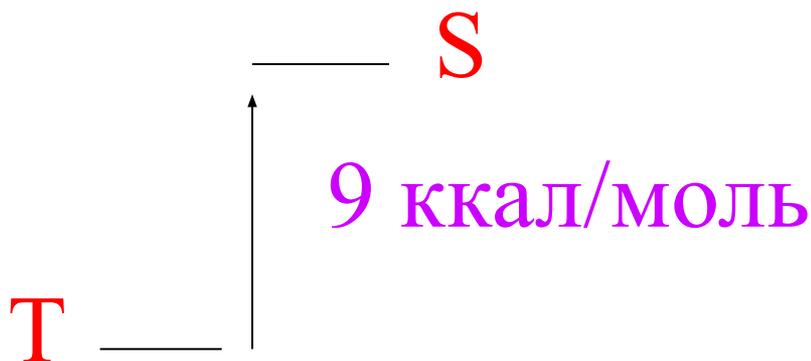


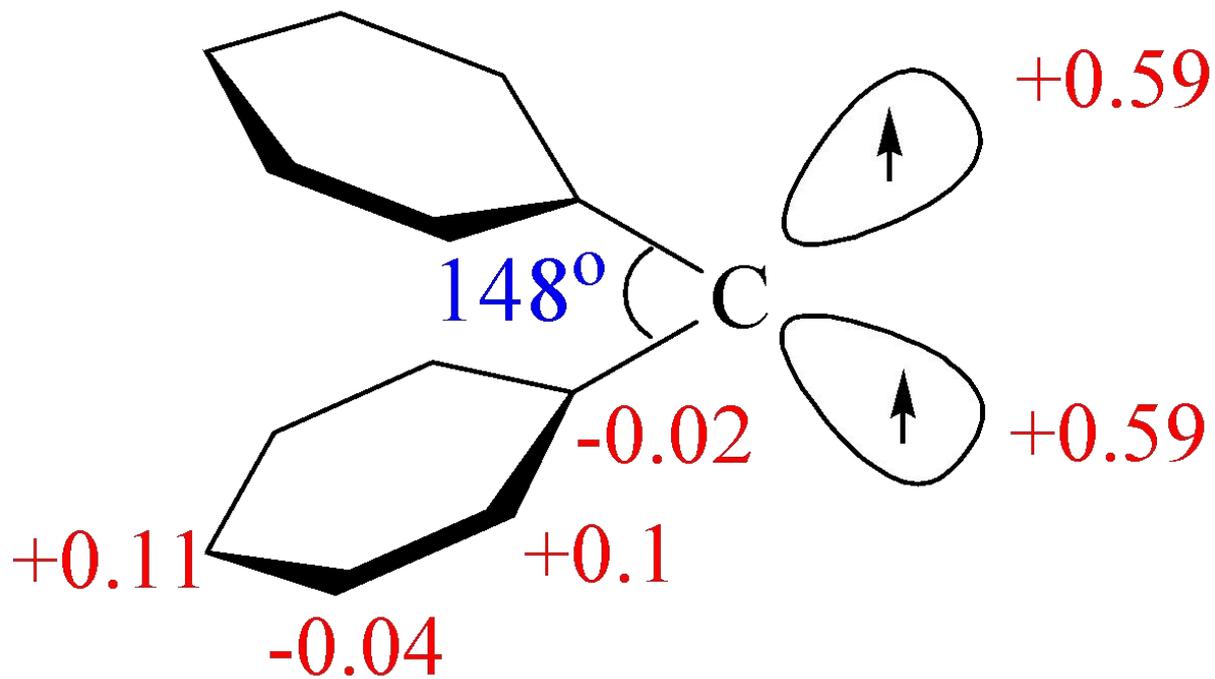
III
 sp (T)

линейная

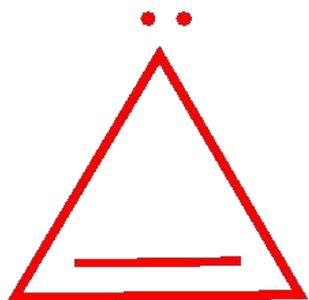


1970 г. метод ЭПР, триплетное состояние

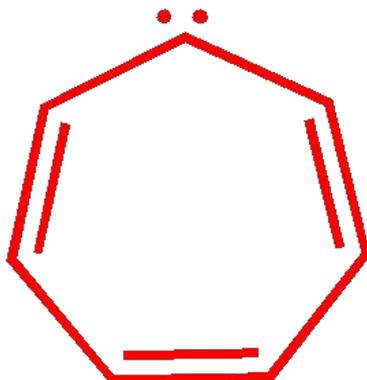




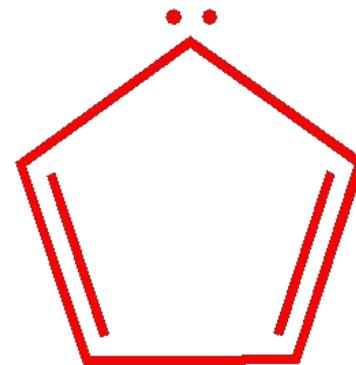
триплетное состояние



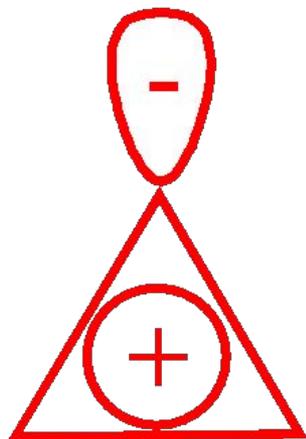
S



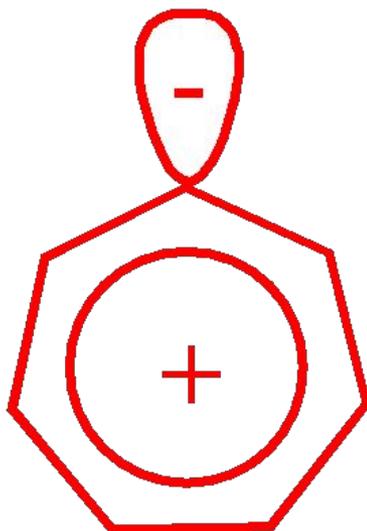
S



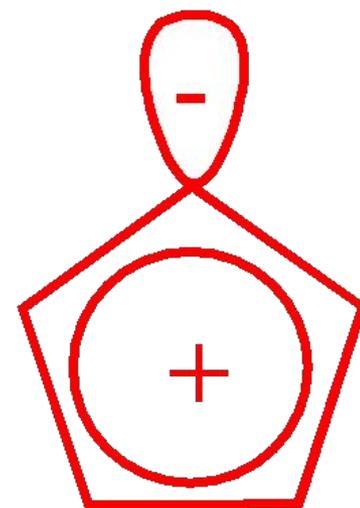
T



аром.

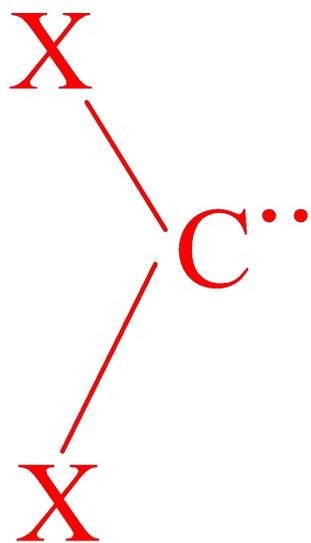


аром.



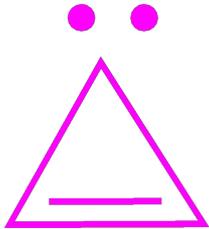
антиаром.

Ab initio STO-3G



X	l_{C-X} , Å	XCX (°)
F	1.323	102.8
OH	1.354	101.9
NH ₂	1.356	109.2
H	1.127	100.2
BH ₂	1.419	180
BeH	1.612	180
Li	1.842	180

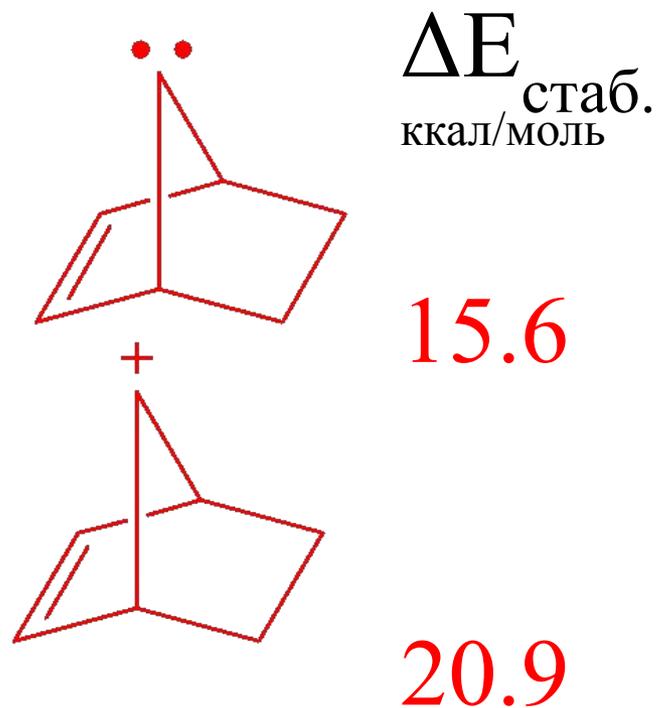
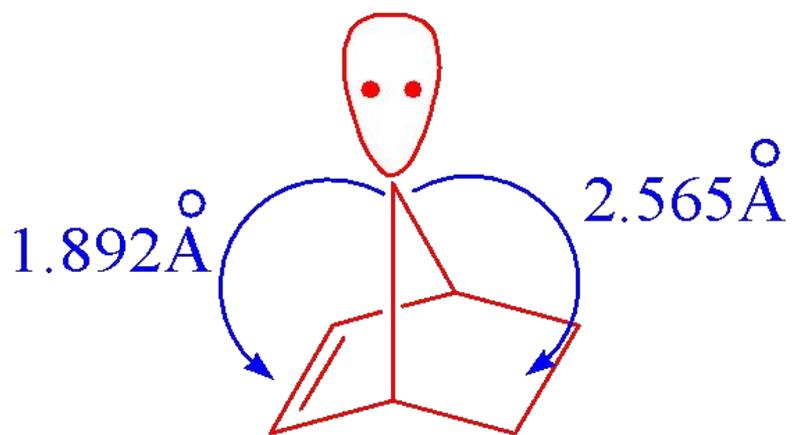
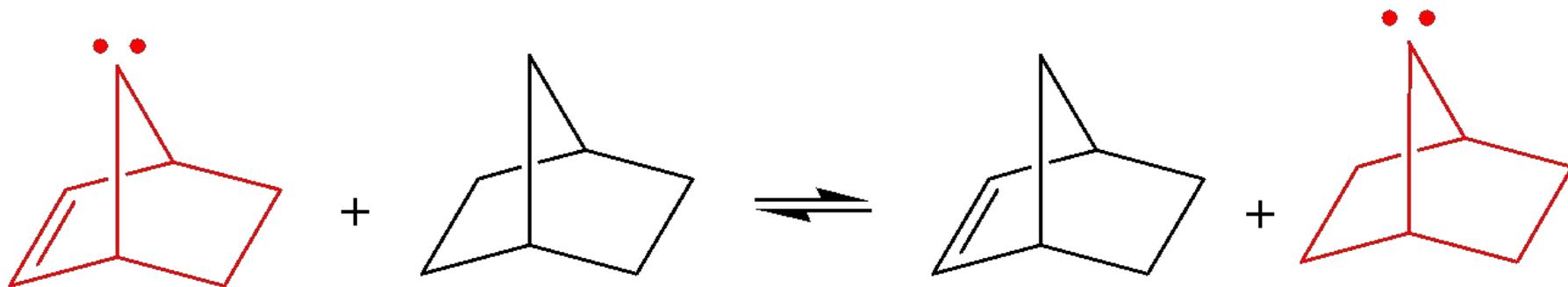
X = C≡CMe линейная конфигурация

	$\Delta E_{ST}'$ ккал/моль		$\Delta E_{ST}'$ ккал/моль
$\text{CH}_2^{\cdot\cdot}$	9	$\text{CF}_2^{\cdot\cdot}$	-54
$\text{Me}_2\text{CH}_2^{\cdot\cdot}$	-2.5	$\text{CCl}_2^{\cdot\cdot}$	-20.8
$\text{H}_2\text{C}=\text{CH}-\text{CH}^{\cdot\cdot}$	6.4		-52
$\text{PhCH}^{\cdot\cdot}$	5.4		
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}^{\cdot\cdot}$	10.3		
$4\text{-HO}_2\text{C}_6\text{H}_4\text{CH}^{\cdot\cdot}$	1.7		
$(\text{H}_2\text{N})_2\text{C}^{\cdot\cdot}$	-53		
$\text{HOCH}^{\cdot\cdot}$	-28		
$\text{FCH}^{\cdot\cdot}$	-14.9		

JACS 2011, 11817

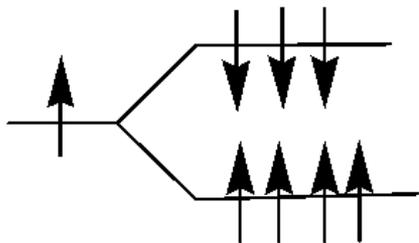
Неклассическое взаимодействие

Изодесмическая реакция (B3LYP/6-31G*)

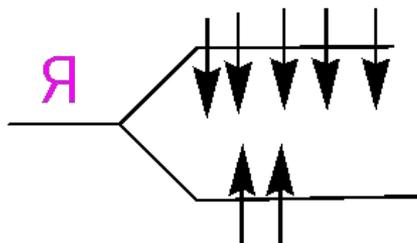
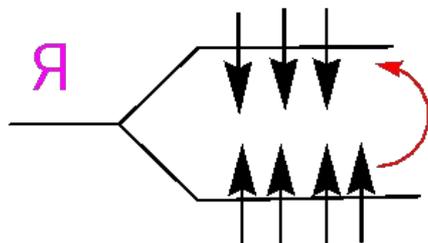
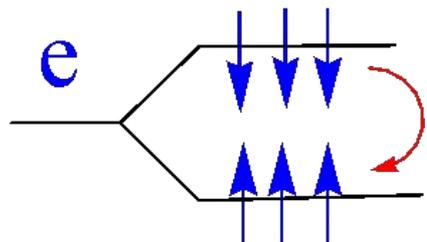


ХЛЧ

ЯМР

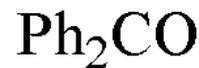
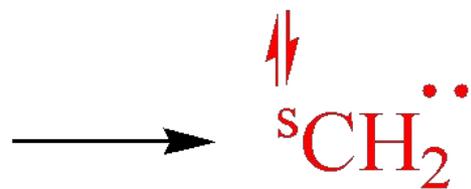
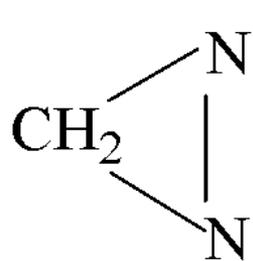


$$I \div (n^+ - n^-)$$

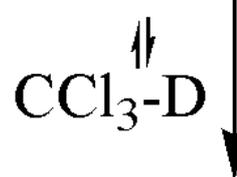
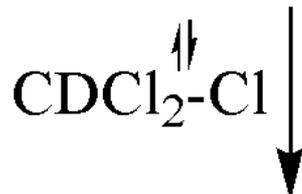


ЭМИССИЯ

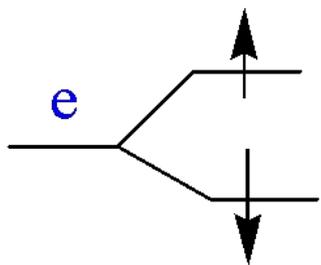
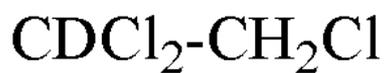




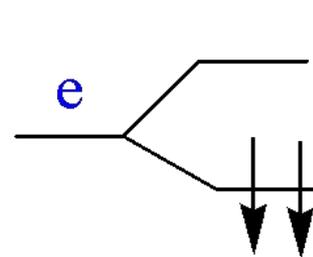
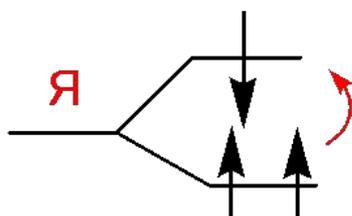
по C-Cl



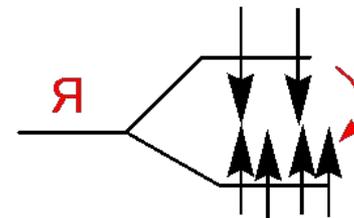
по C-D



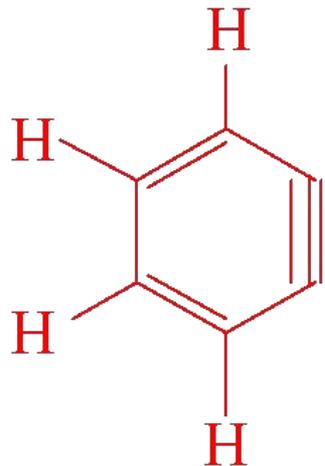
ЭМИССИЯ



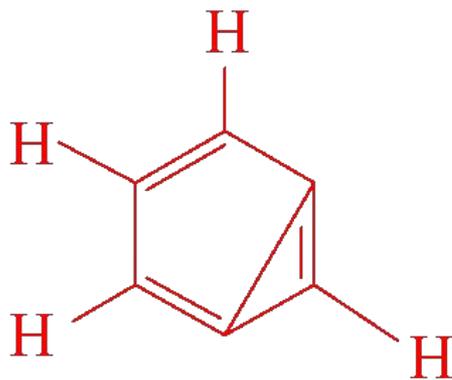
увеличение
ИНТЕНСИВНОСТИ



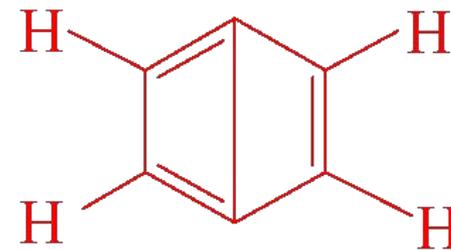
Арины



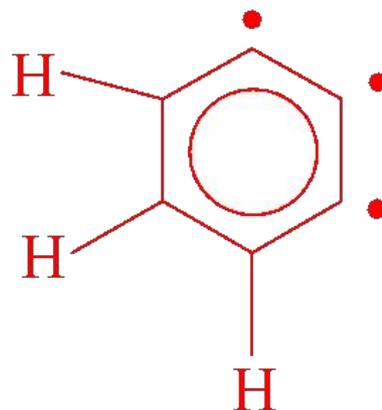
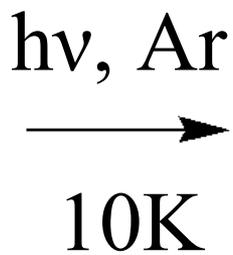
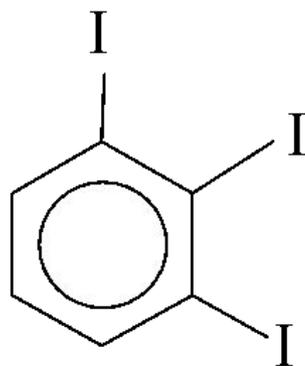
орто-дегидро-
бензол



мета-дегидро-
бензол

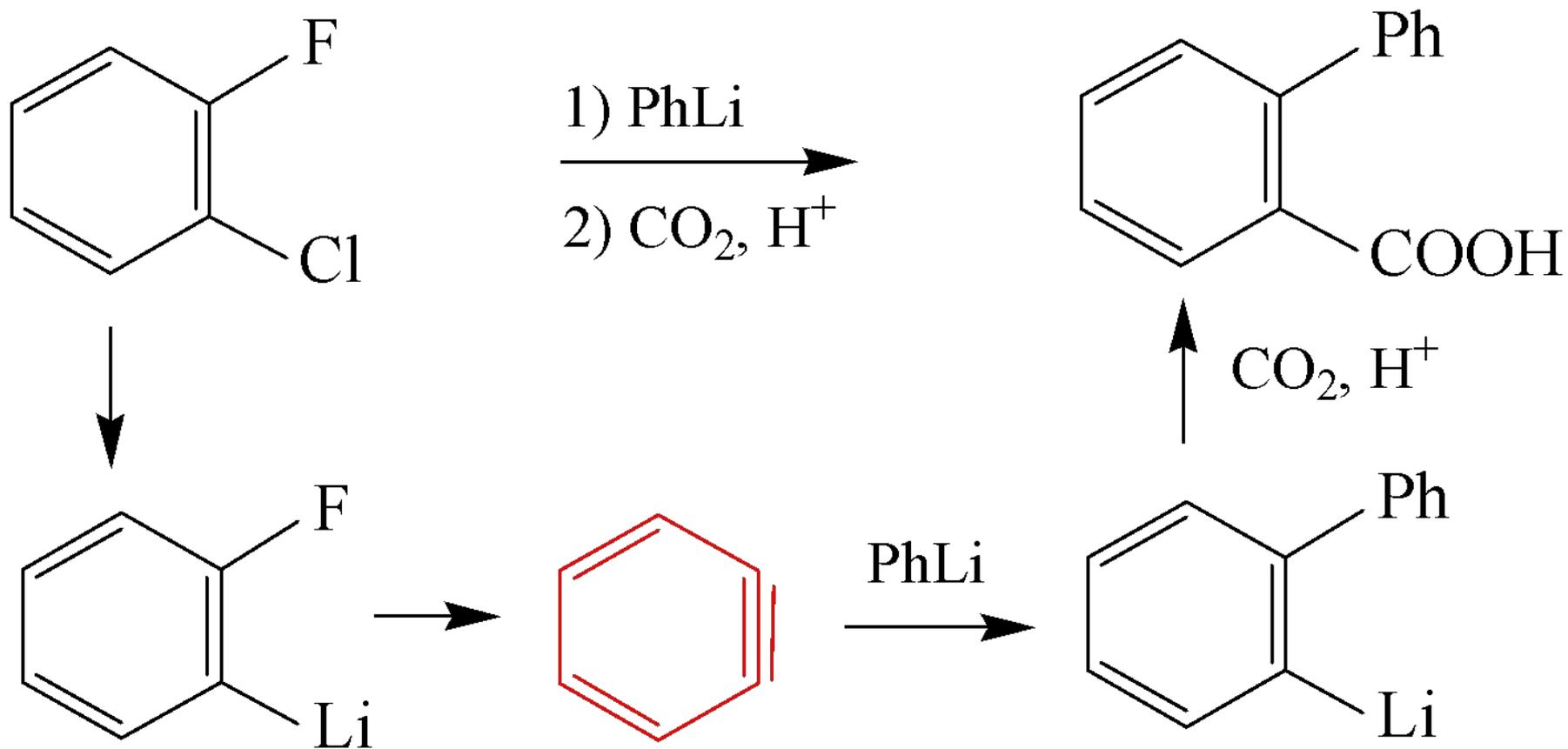


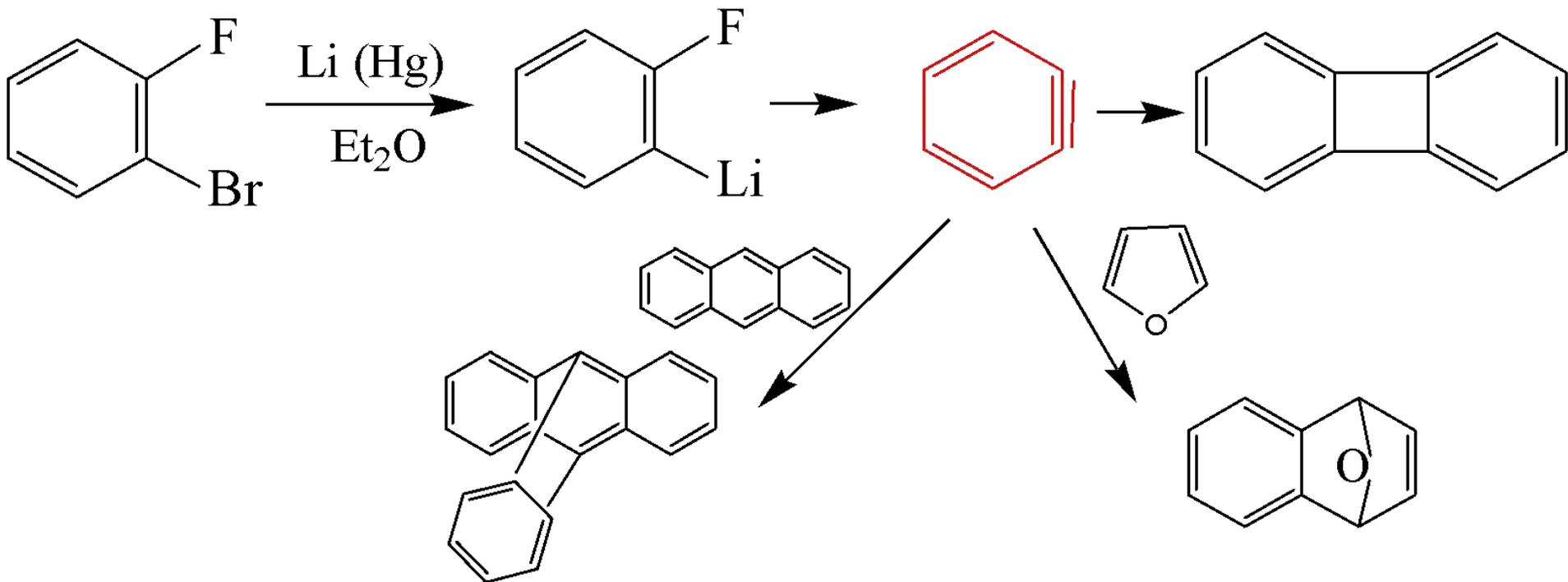
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бензол



W. Sander
Ang. Chem. Int.
2005, 6306

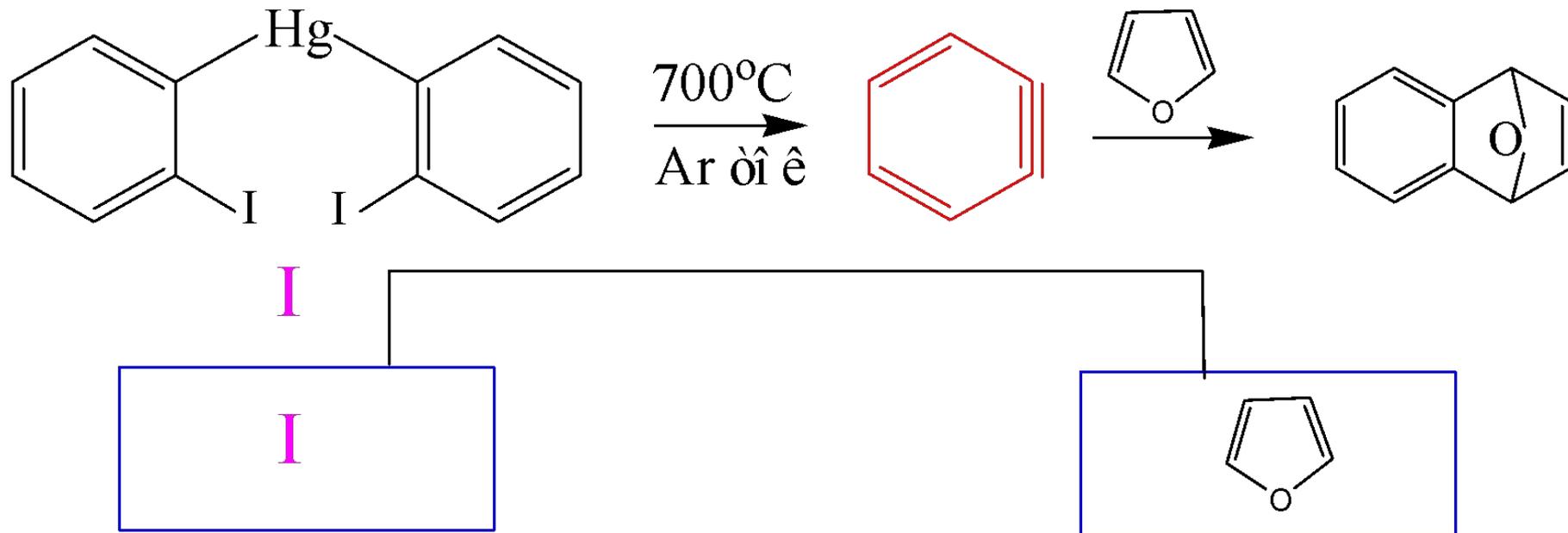
1942 г. Wittig





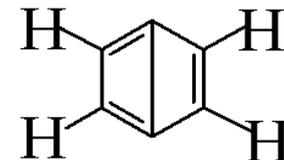
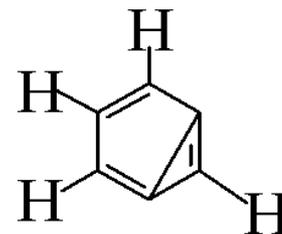
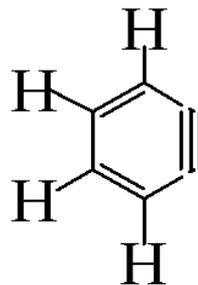
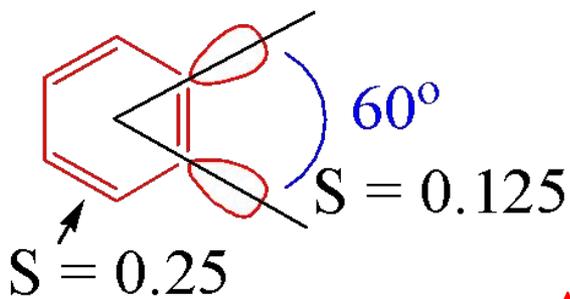
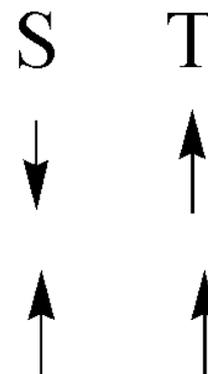
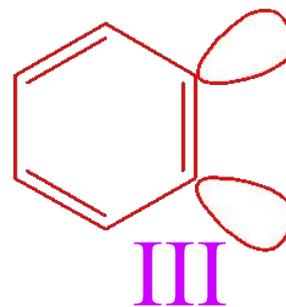
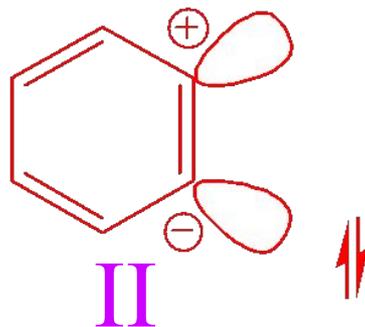
триптицен
(12 стадий)

Дегидробензол - частица



цвиттер-ион

бирадикал



$\Delta H_{\text{обр.}}$
158

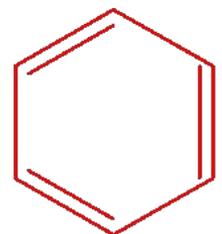
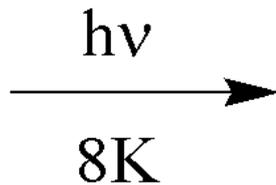
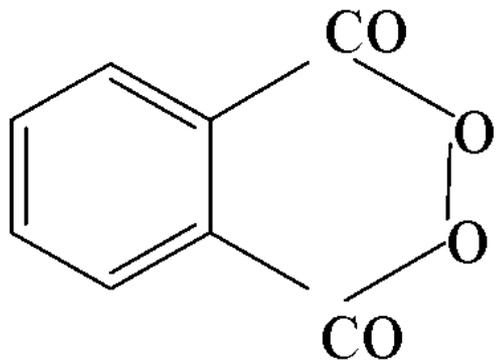
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137

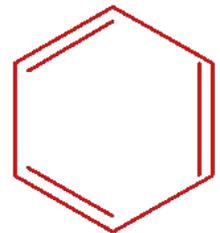
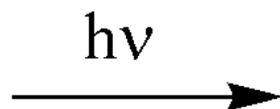
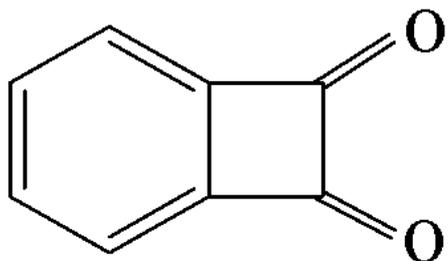
ккал/моль

Расчет MNDO

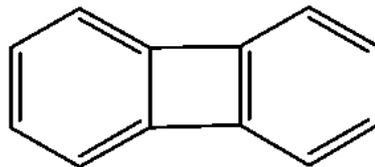
По ИКС C_{2v}



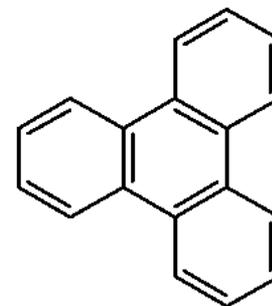
+ 2CO



+ 2CO



+



Другие арины и гетарины

слабое перекрывание

