

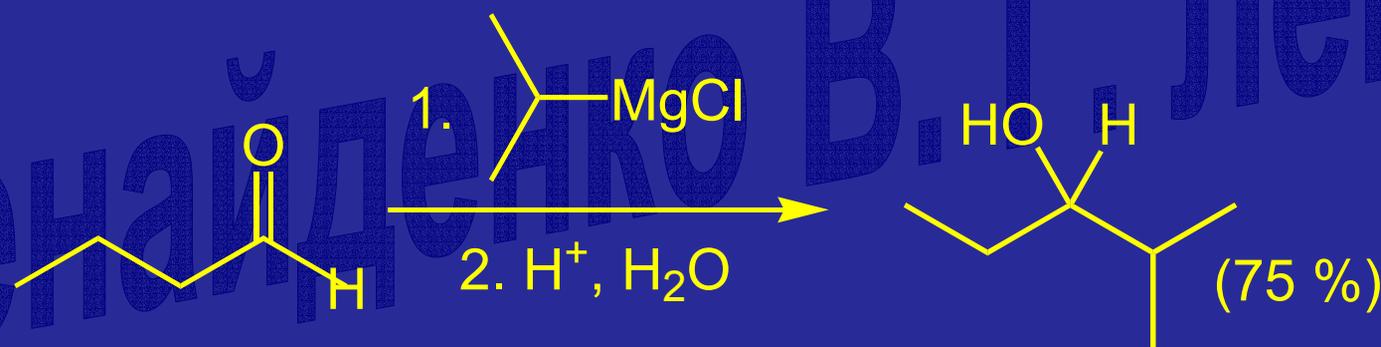
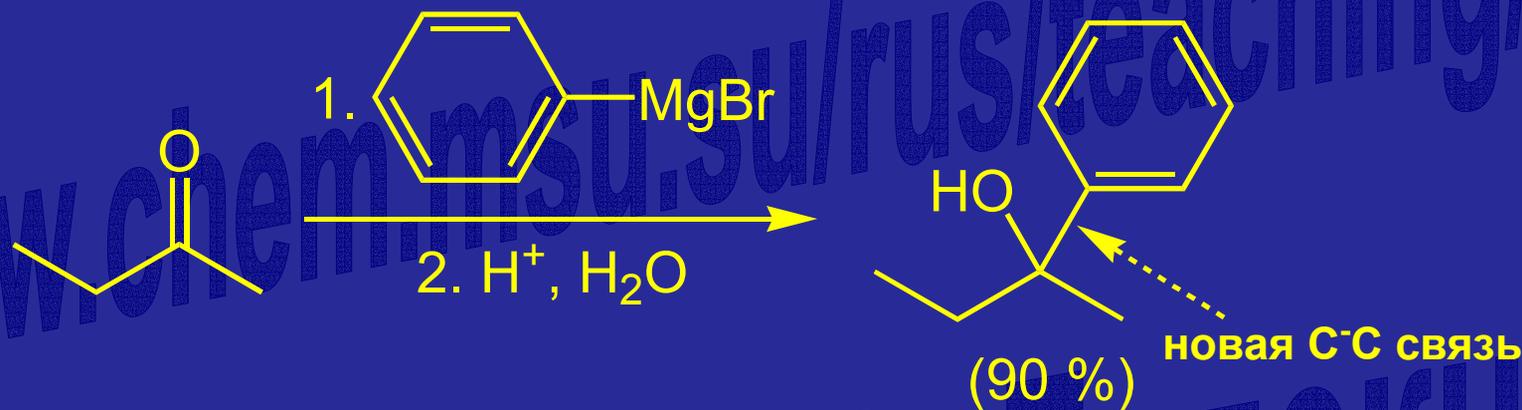
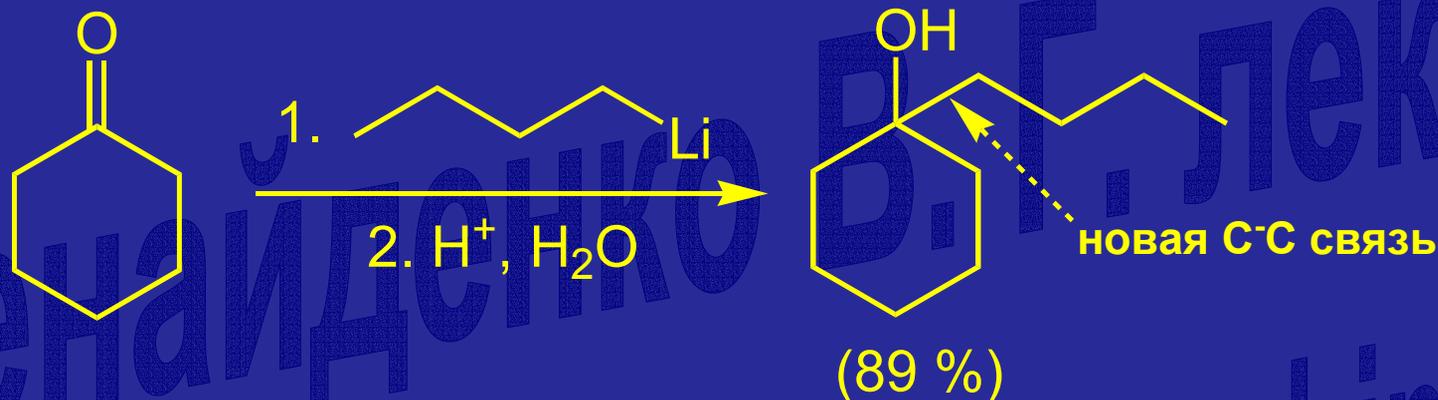
Лекция 25

Карбонильные соединения. Реакция нуклеофильного присоединения

- ◆ Scientia difficilis, sed fructuosa
- ◆ Знание трудно, но плодотворно

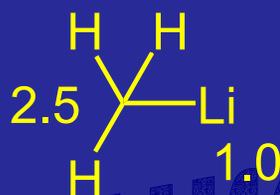
- ◆ Реакции альдегидов и кетонов с металлоорганическими соединениями.
- ◆ Магнийорганические соединения. Методы синтеза: взаимодействие металла с алкил- или арилгалогенидами. Строение реактивов Гриньяра, равновесие с диалкилмагнием. Этинильные производные — реактивы Иочича. Магнийорганические соединения в синтезе углеводородов, спиртов (первичные, вторичные, третичные), альдегидов, кетонов, карбоновых кислот.

Присоединение металлоорганики по СО группе

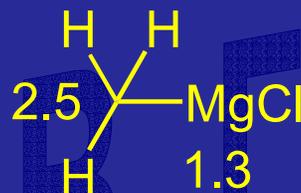


Электроотрицательность атомов

H 2.1							
Li 1.0	Be 1.6			C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.3			Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8		Cu 1.9	Zn 1.7		As 2.0	Se 2.4	Br 2.8
							I 2.5



ИОННОСТЬ СВЯЗИ 43%



35%

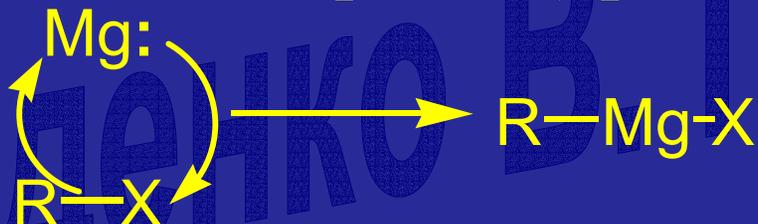
Реактивы Гриньяра

В. Гриньяр Нобелевская премия 1912 г.



Получение реактивов Гриньяра

Окислительное внедрение (присоединение) магния



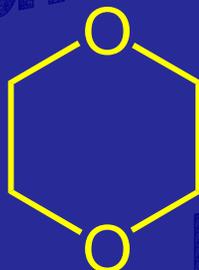
комплекс между
кислотой Льюиса -
ионом металла и ТГФ



диэтиловый эфир



тетрагидрофуран

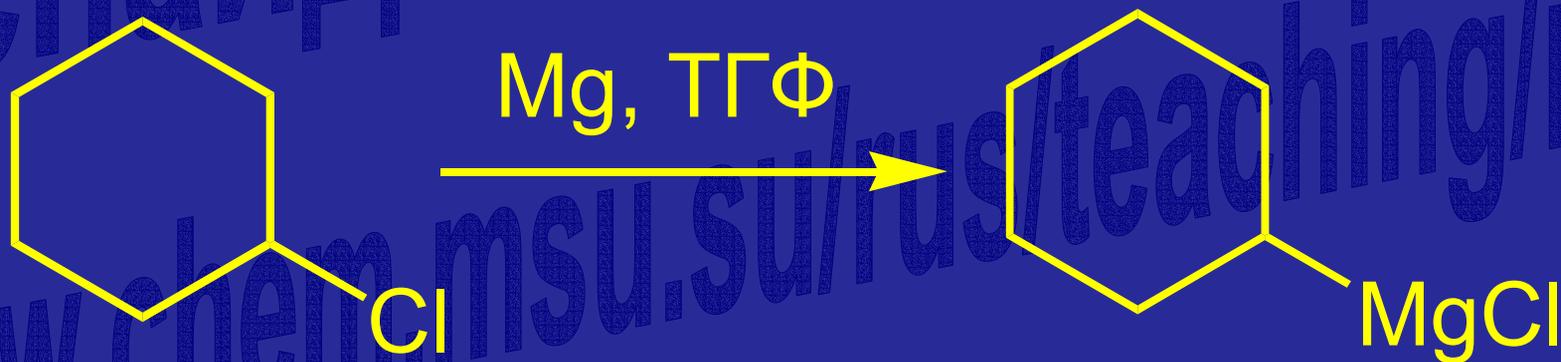


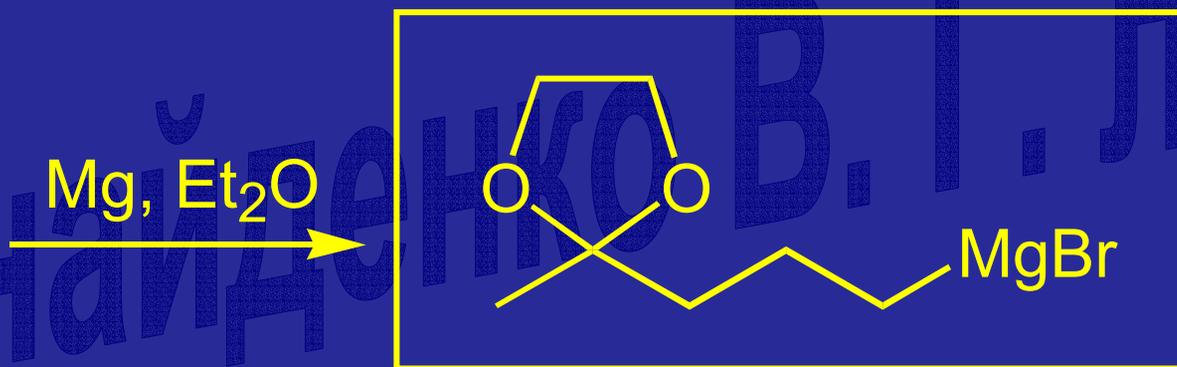
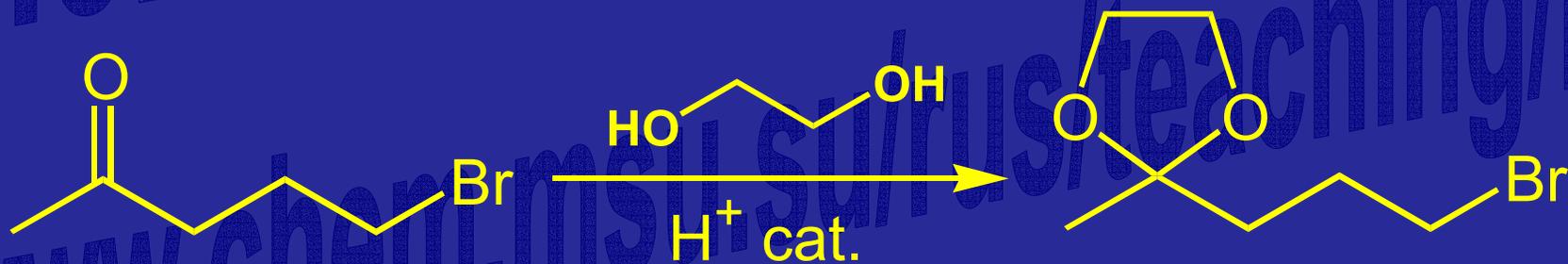
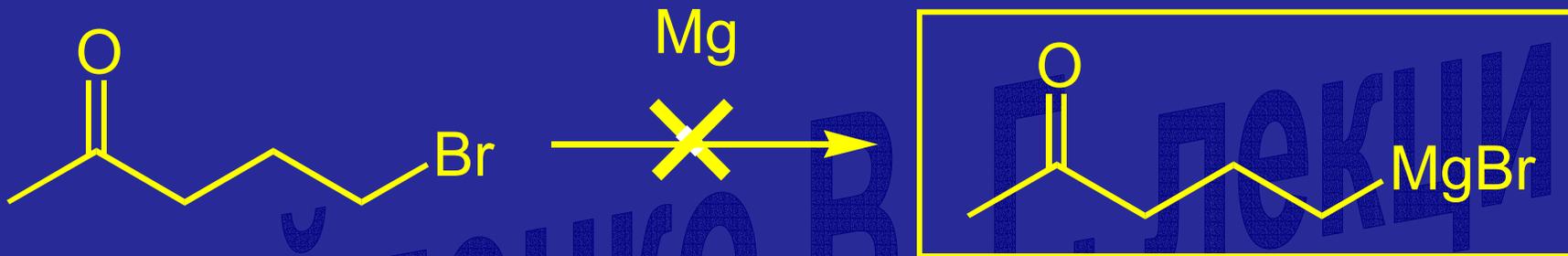
диоксан



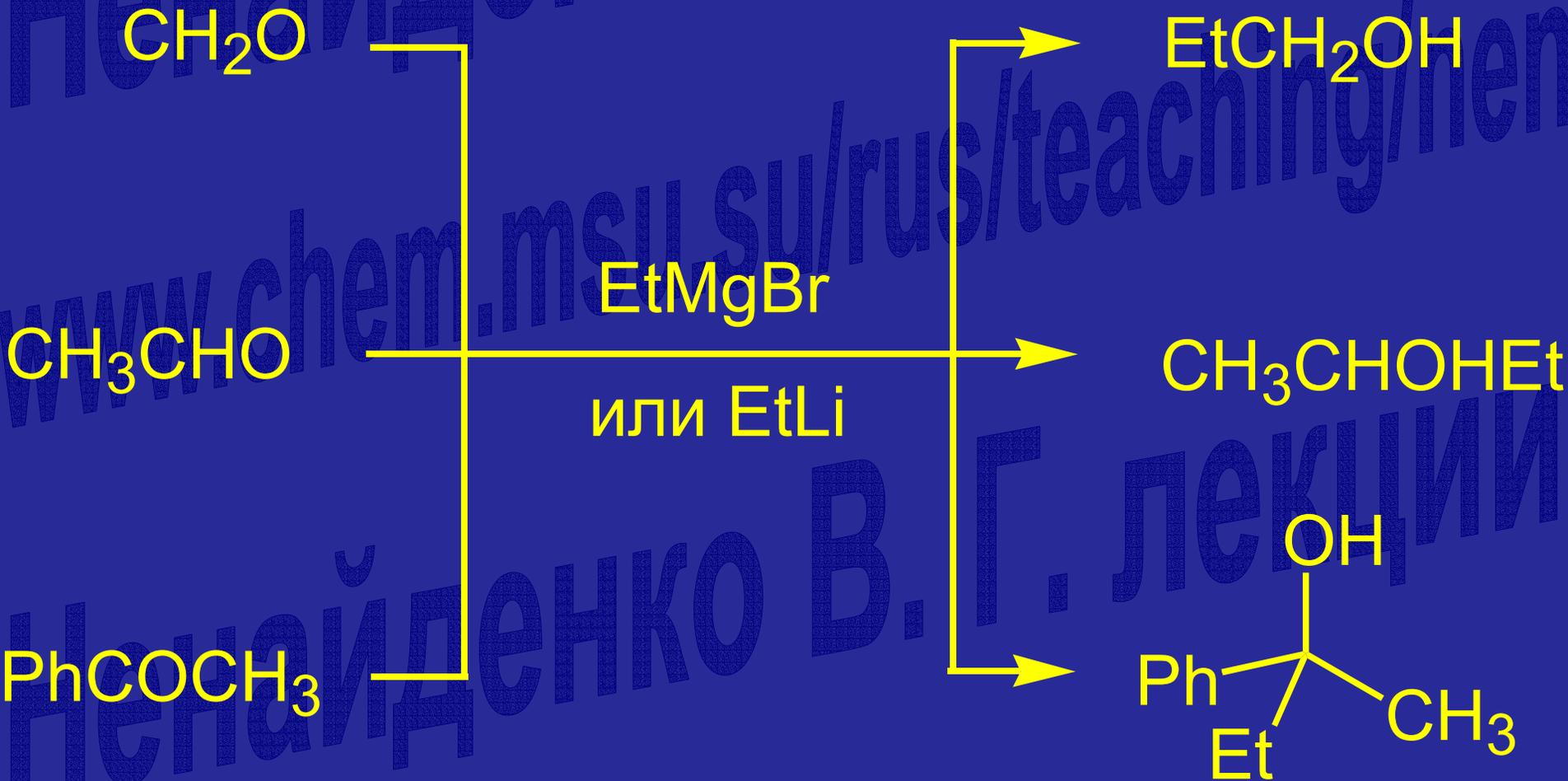
ДМЭ, диметоксиэтан

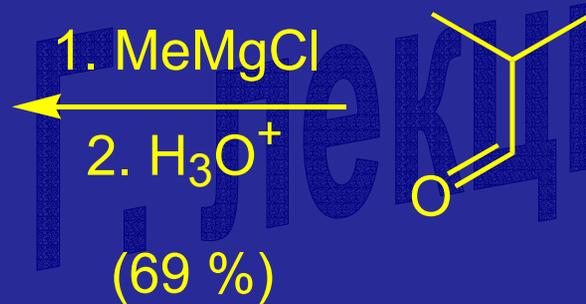
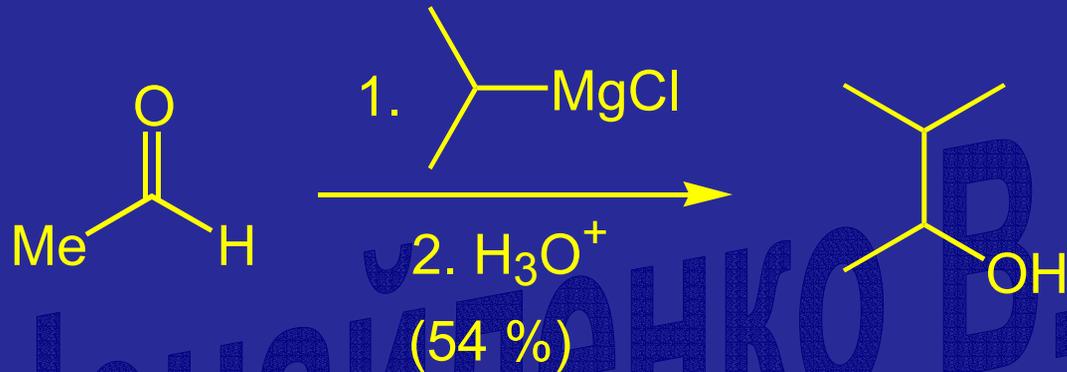




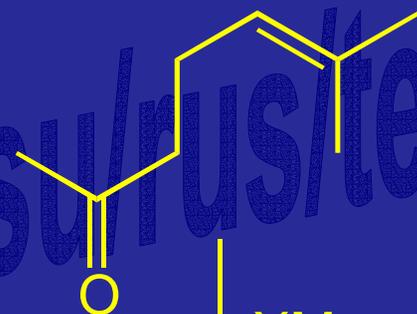
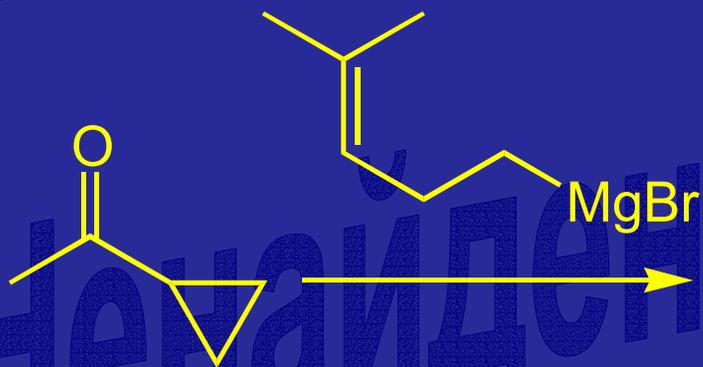


Получение спиртов из альдегидов и кетонов

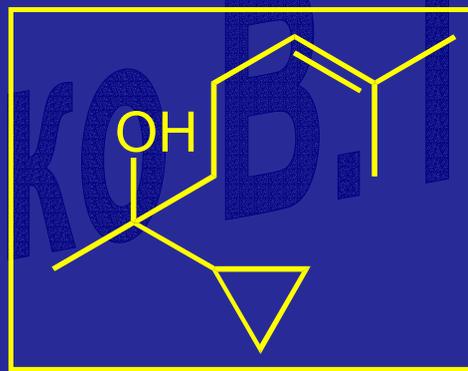




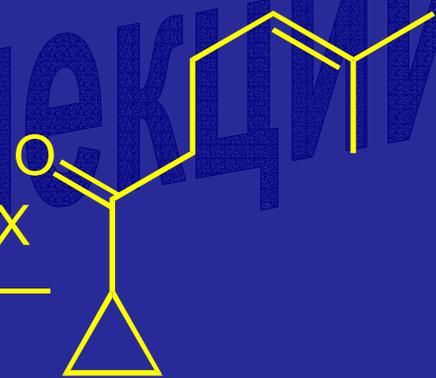
$\text{Mg, Et}_2\text{O}$



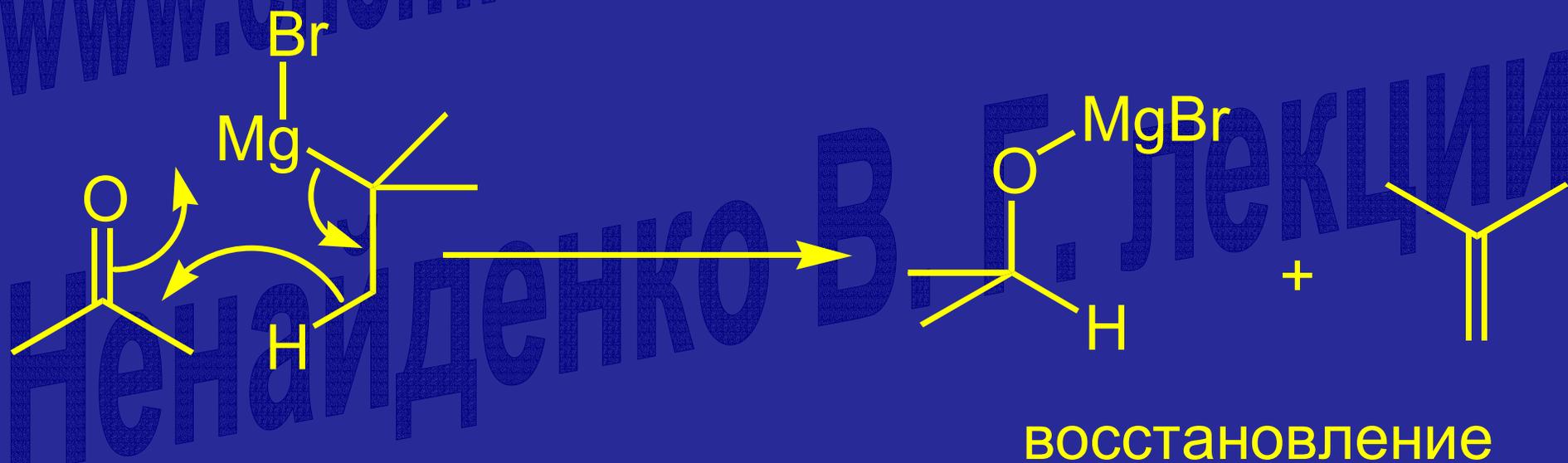
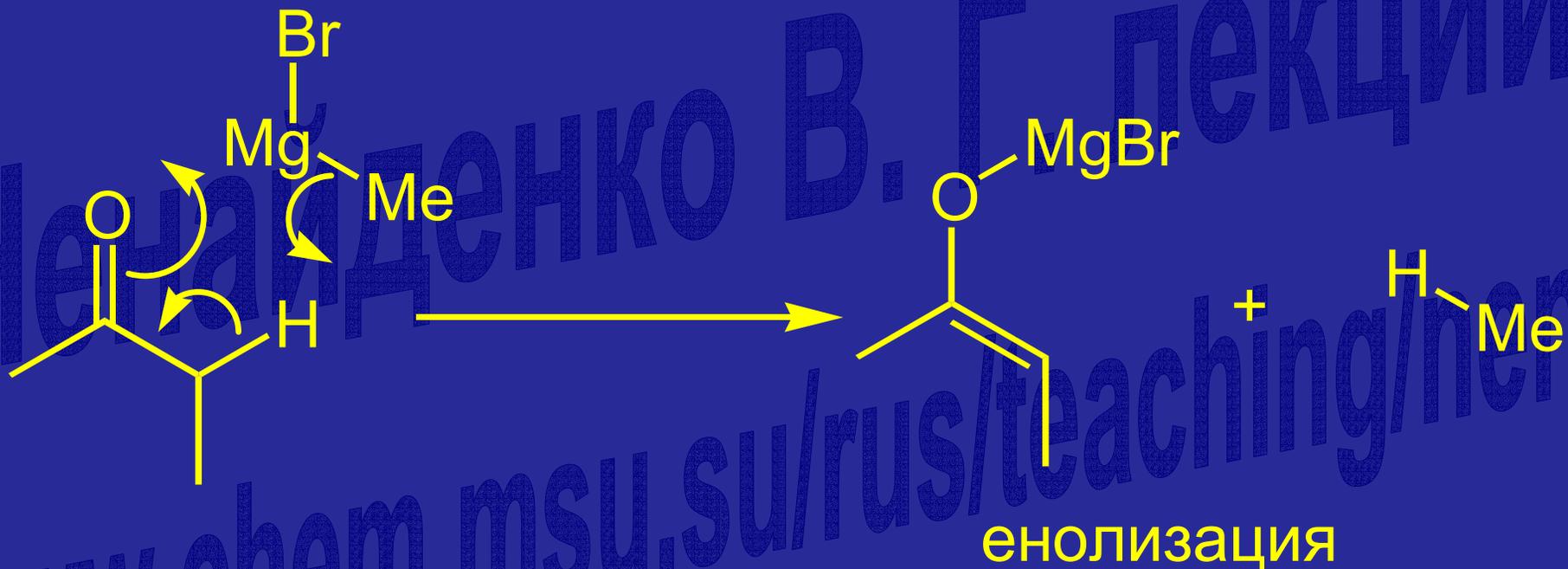
XMg - C1CC1



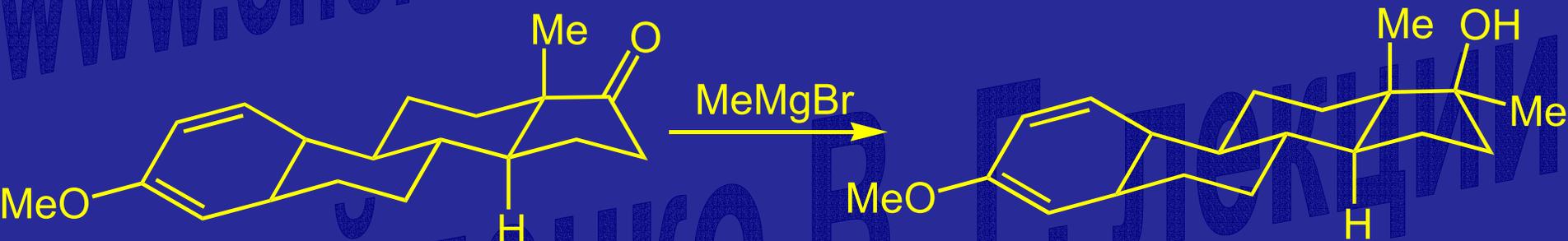
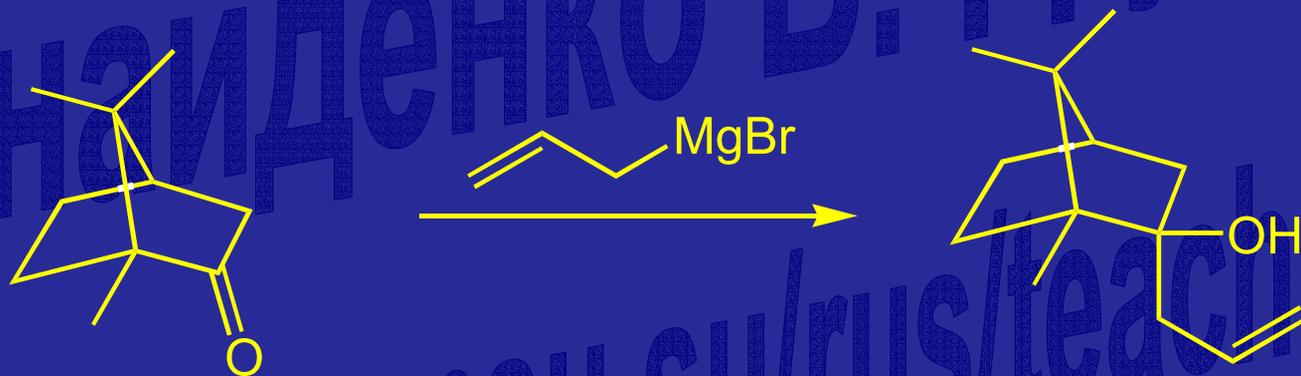
MeMgX



Побочные реакции

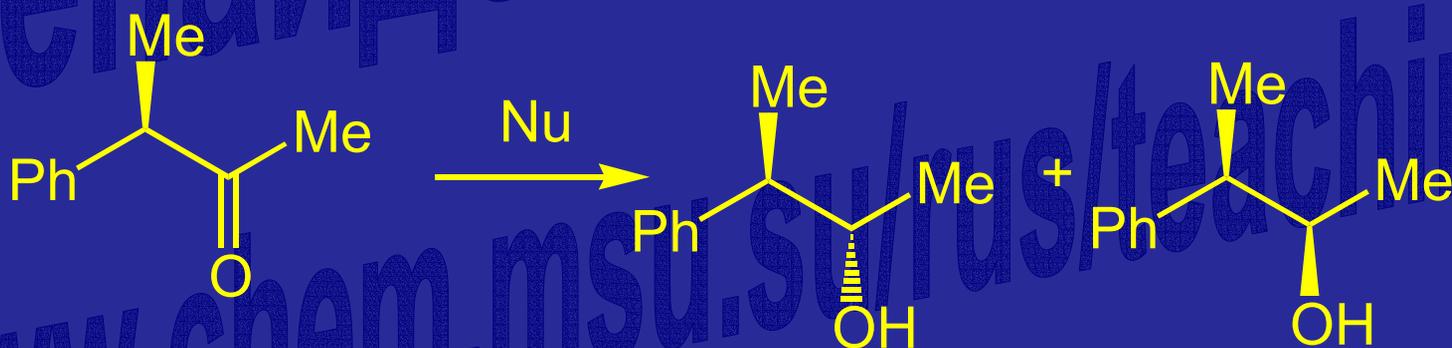


Сtereoхимия присоединения

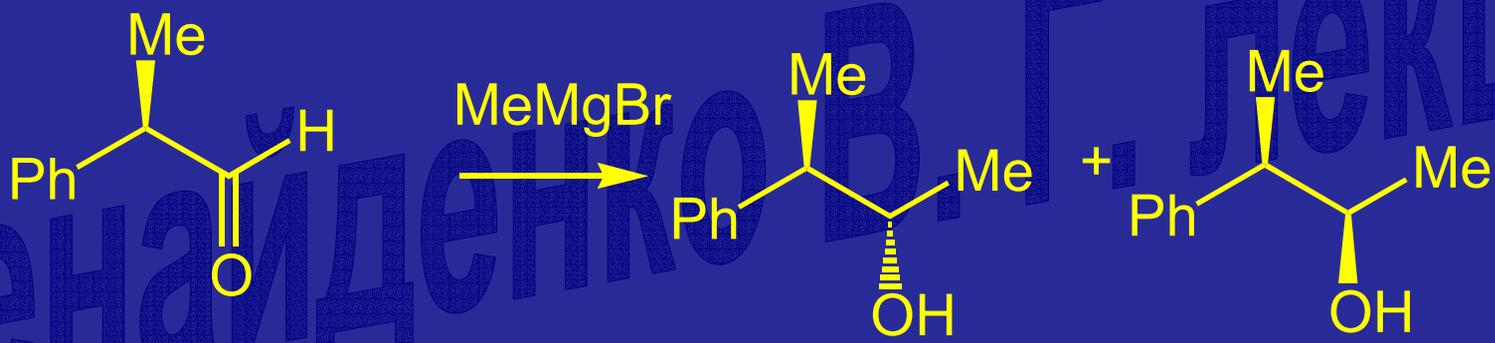




R	соотношение диастереомеров
Me	74/26
Et	76/24
iPr	83/17
tBu	98/2



LiAlH ₄	74	26
LiBH(sBu) ₃	>99	<1



34	66
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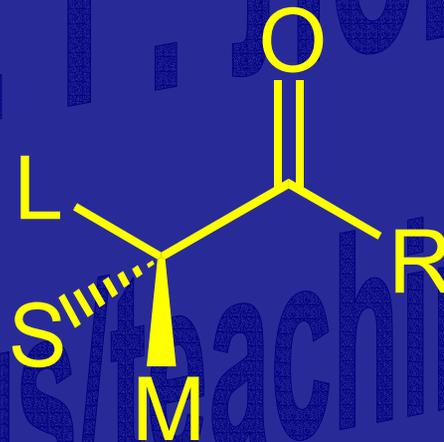
Модель Felkin-Anh

наиболее важные конформации

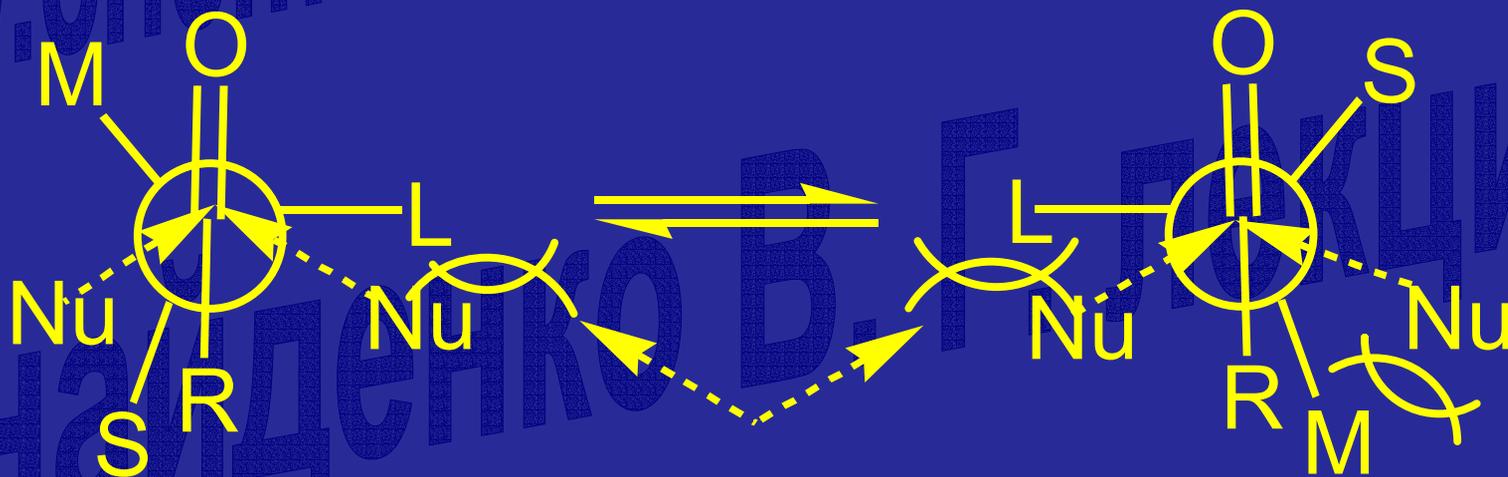
L - большая

M - средняя

S - малая



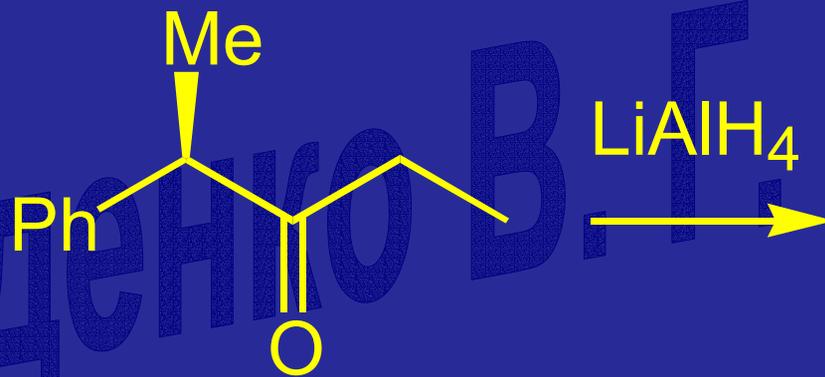
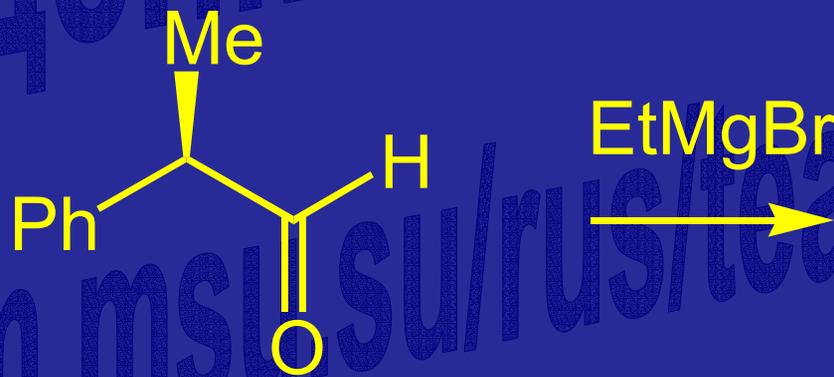
нуклеофил подходит под углом 107°



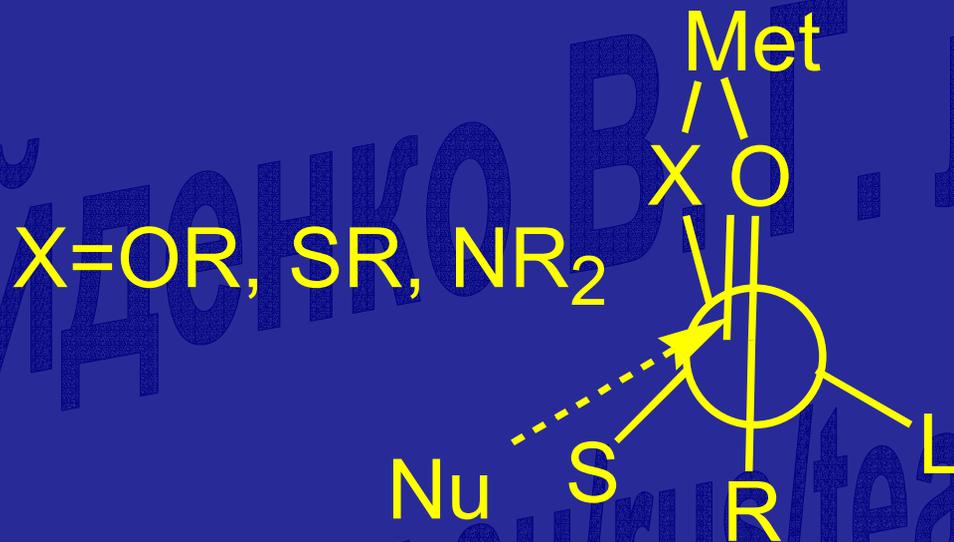
стерические препятствия

Задание на дом

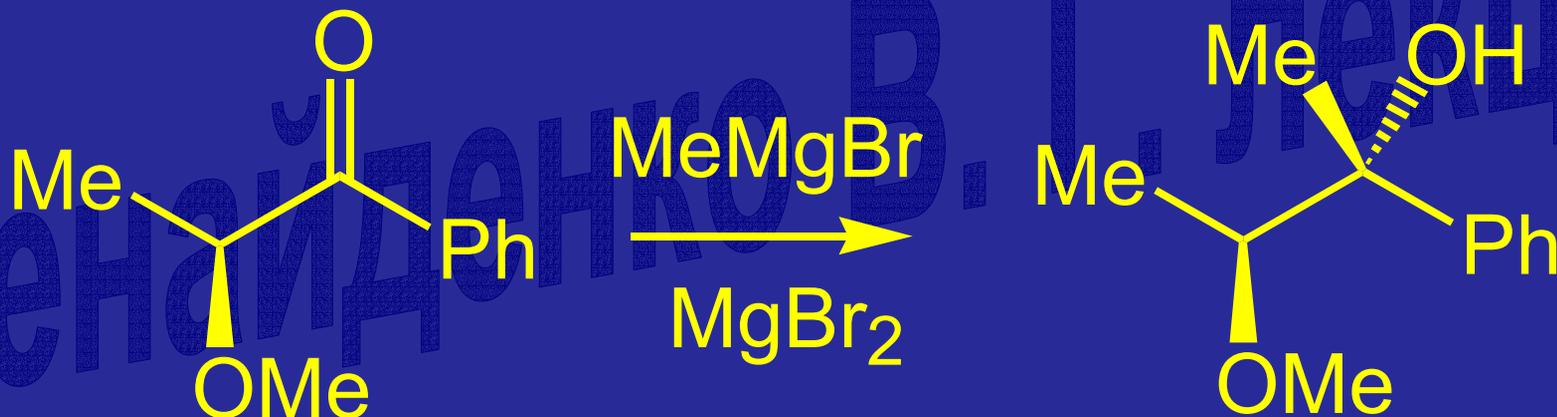
предскажите структуру основного диастереомера,
используя модель Felkin-Anh

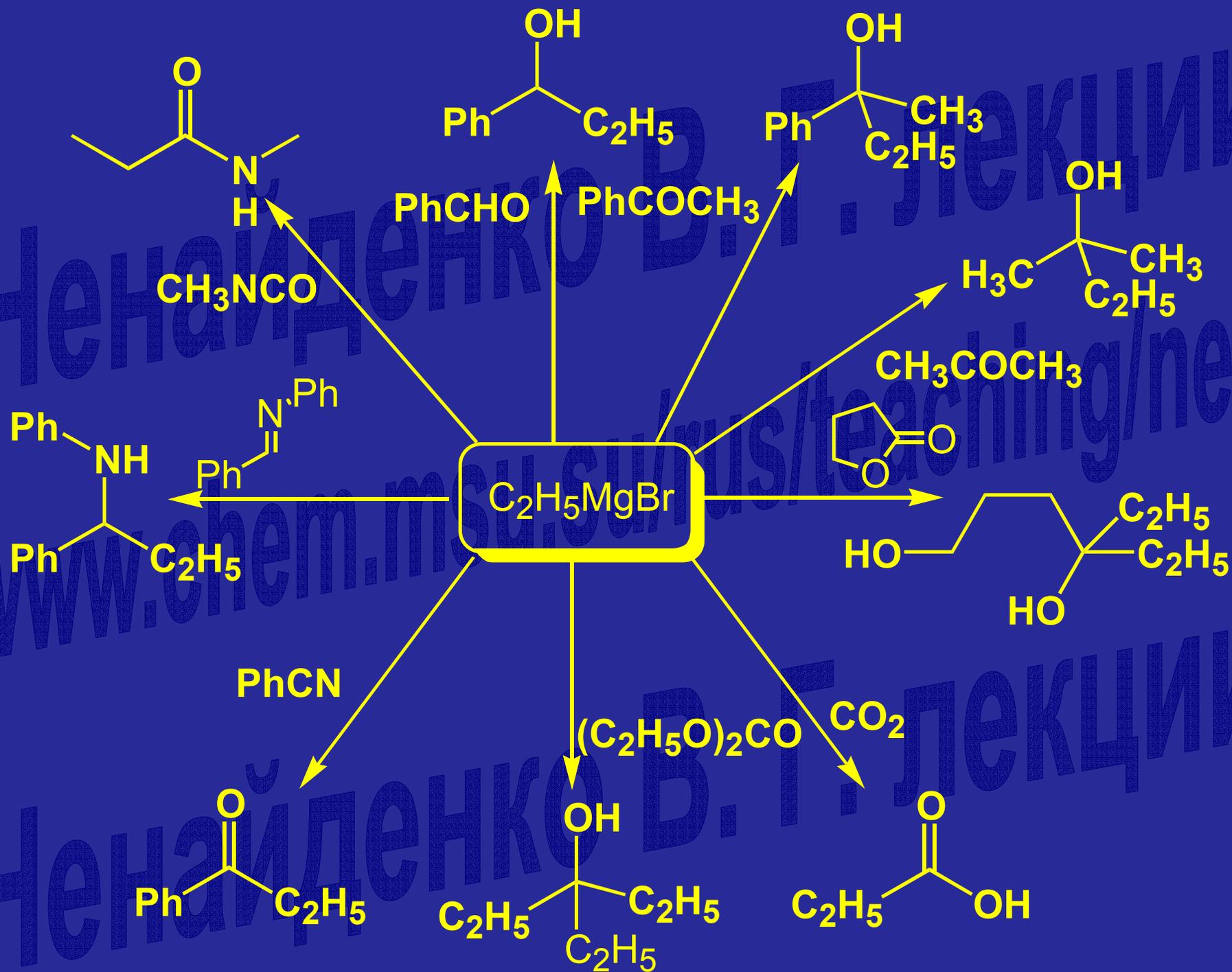


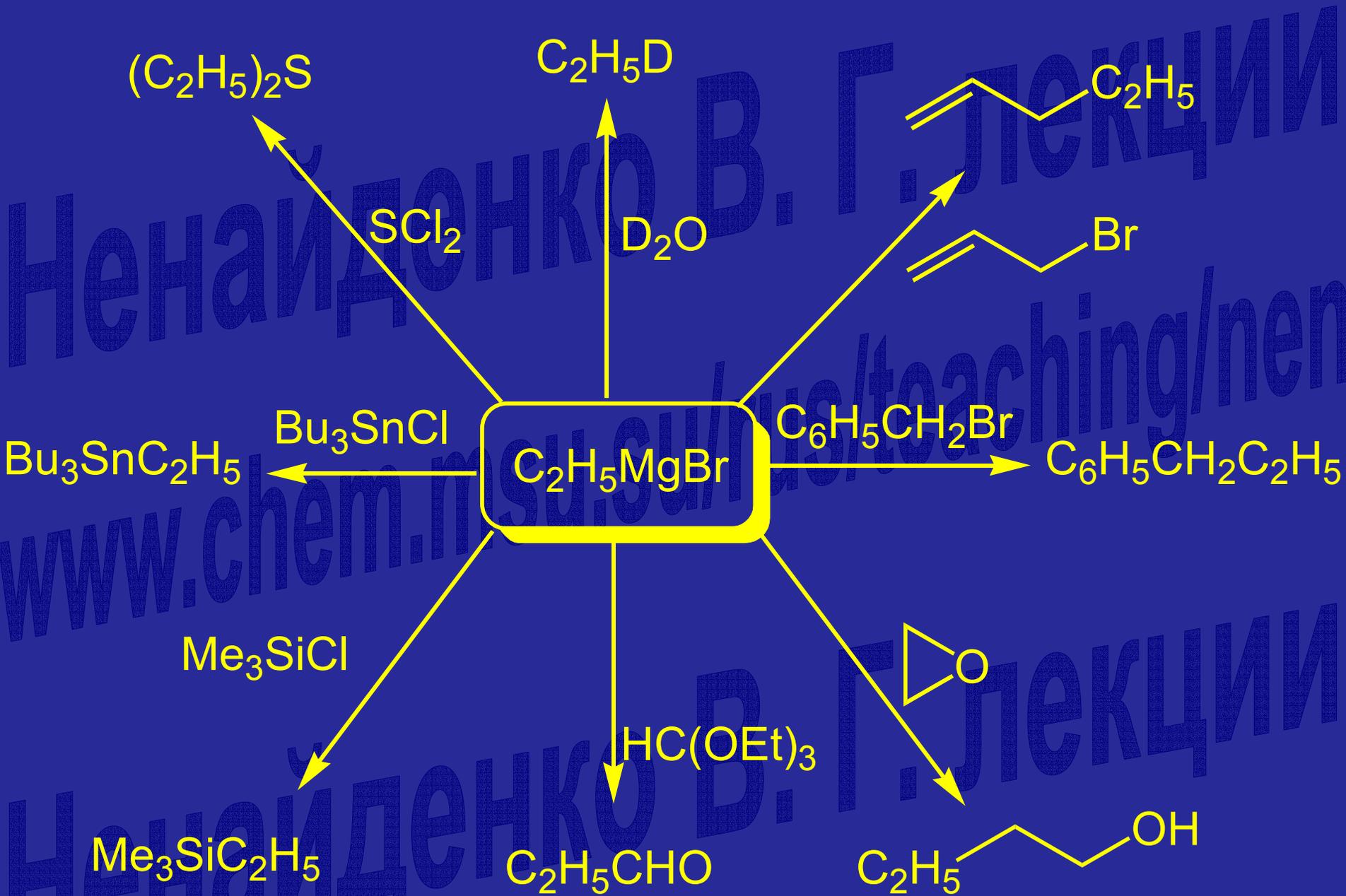
Контроль стереохимии за счет хелатирования



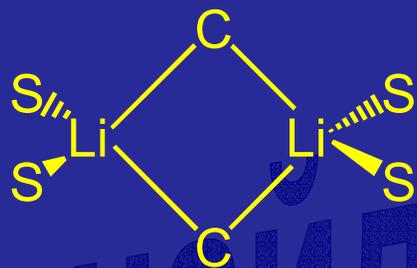
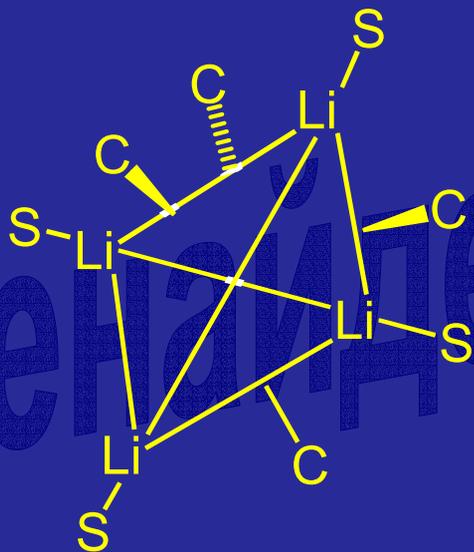
предпочтительный
подход нуклеофила



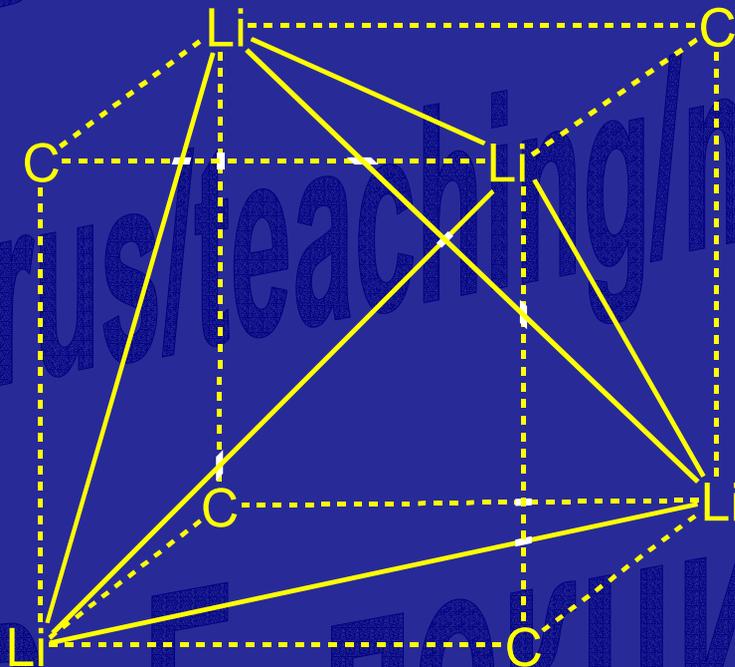


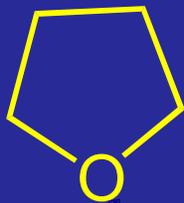


Литийорганические производные



C = Bu
S = TГФ





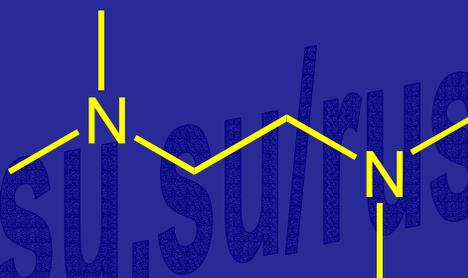
THF



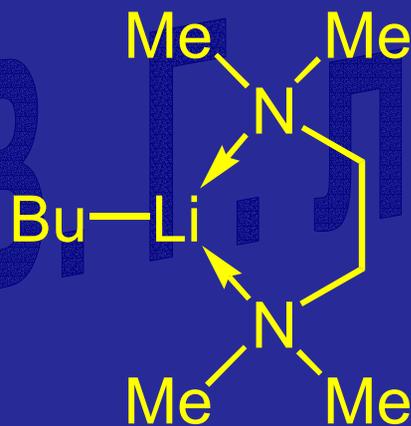
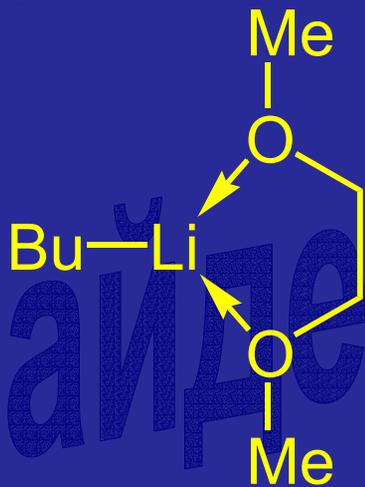
DME



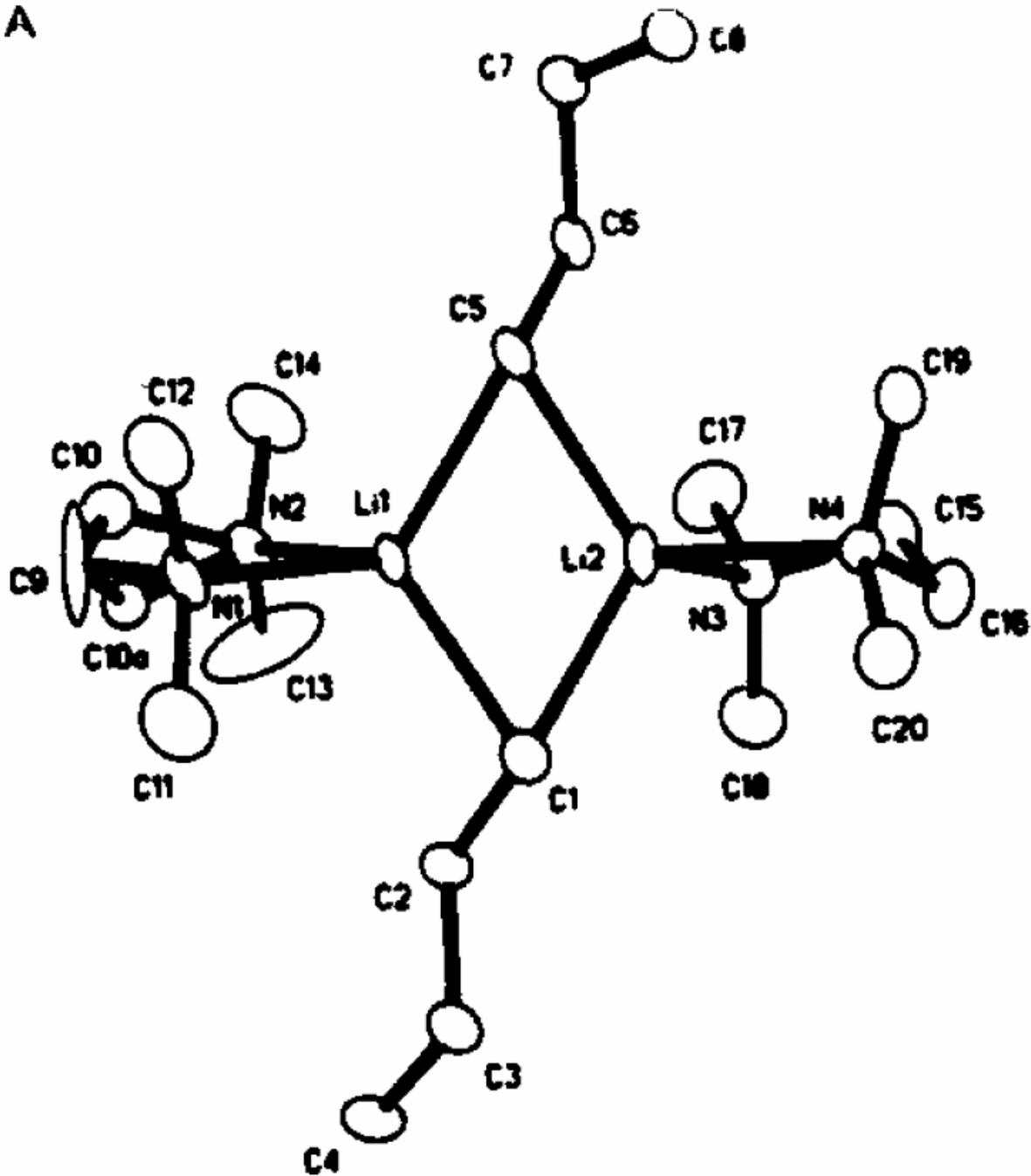
DABCO



TMEDA

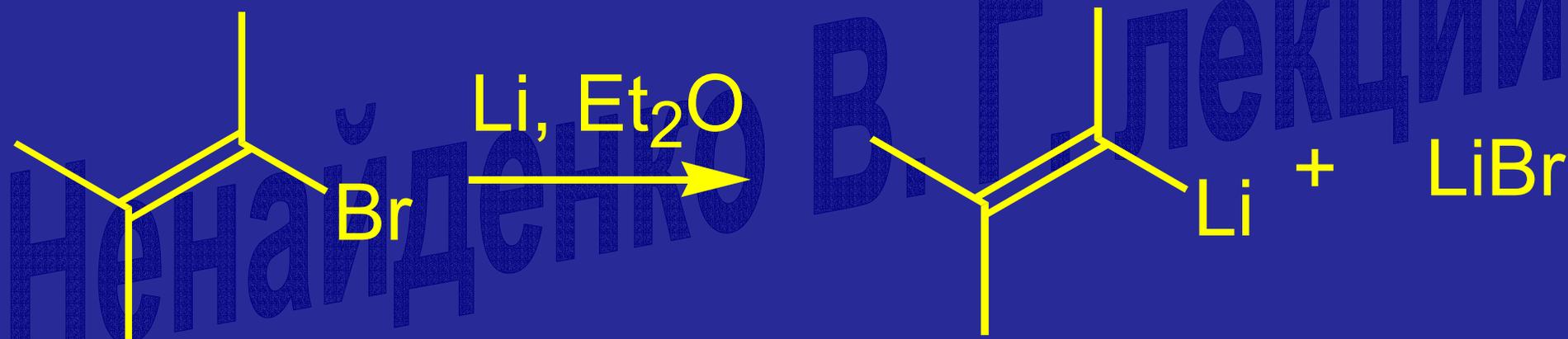
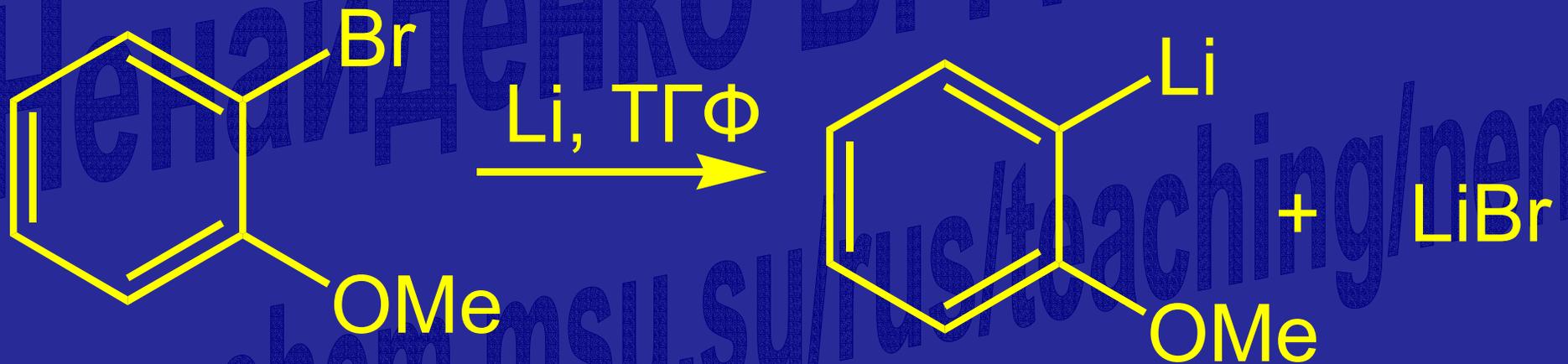


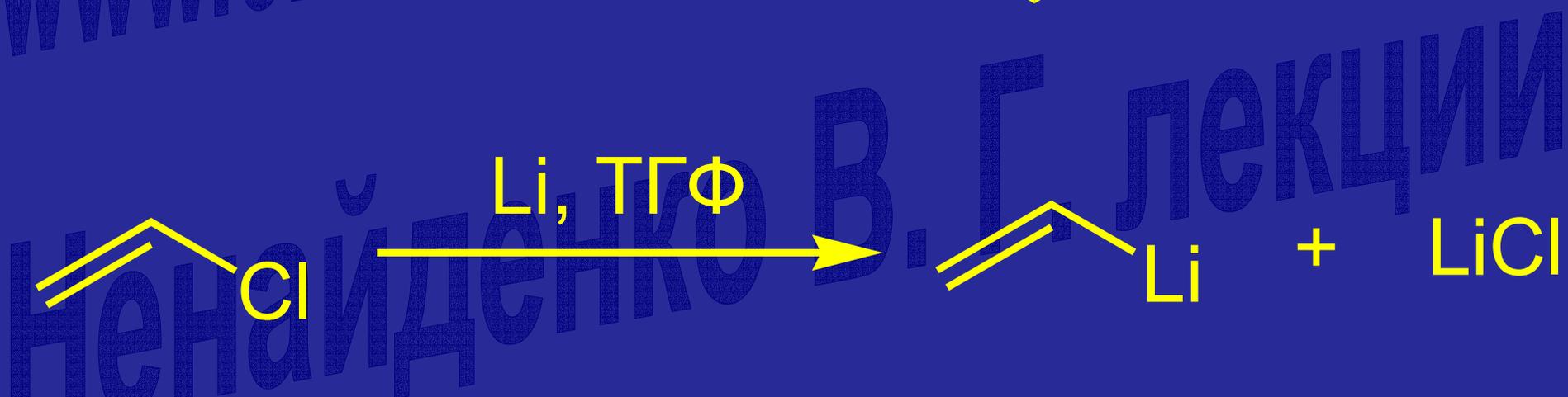
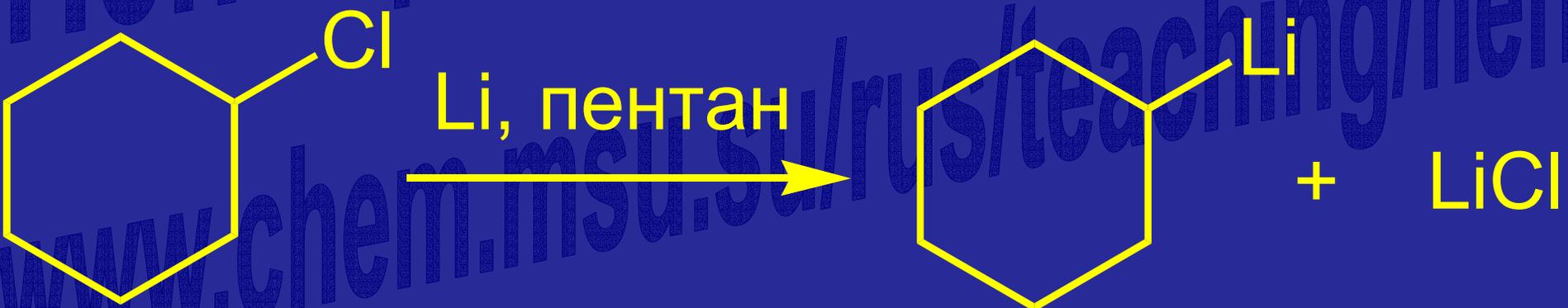
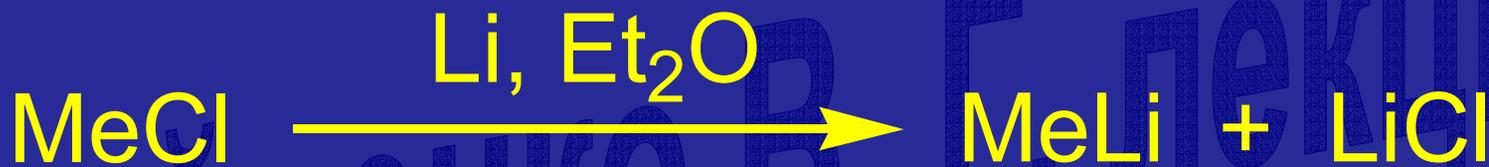
A



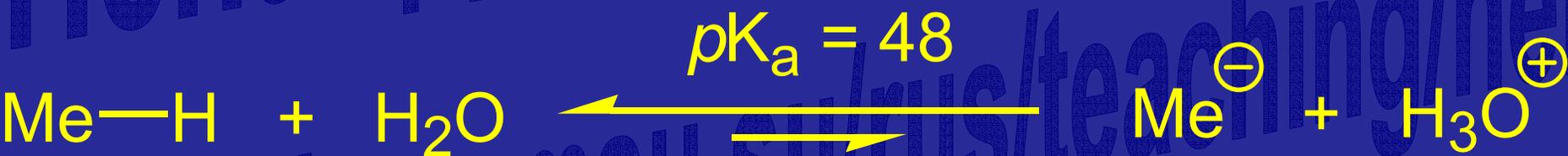
Синтез литийорганических соединений.

Внедрение лития по связи C-Hal

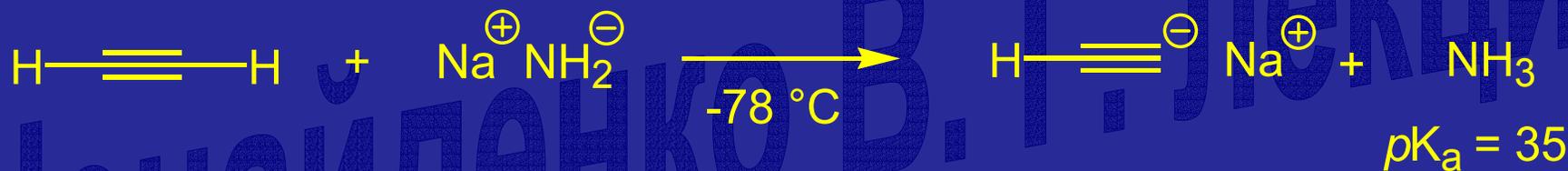
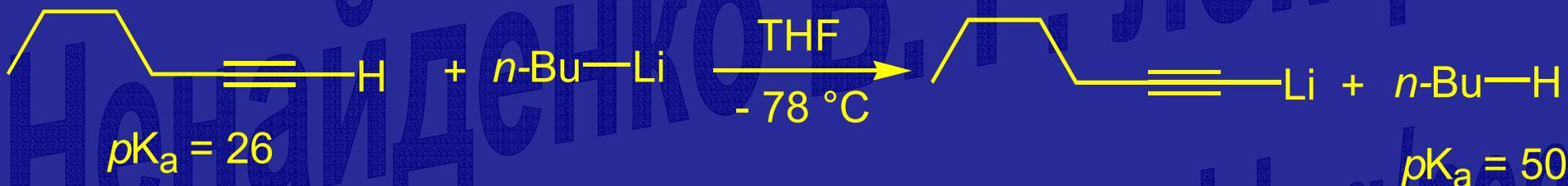


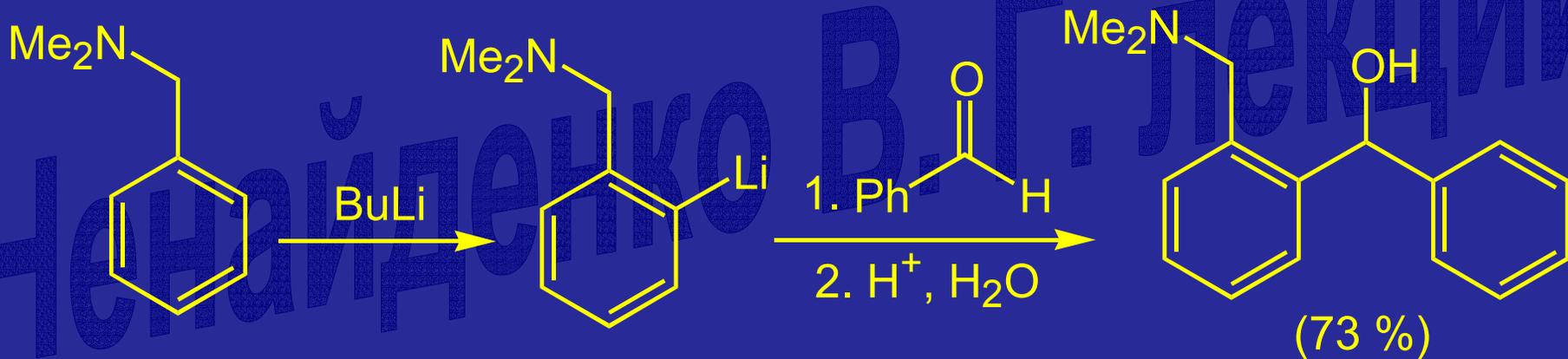
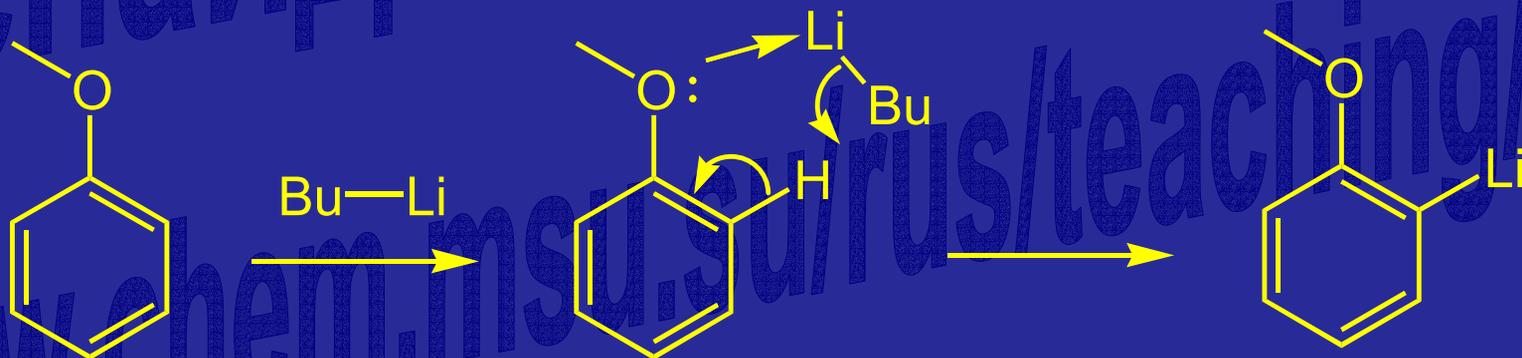
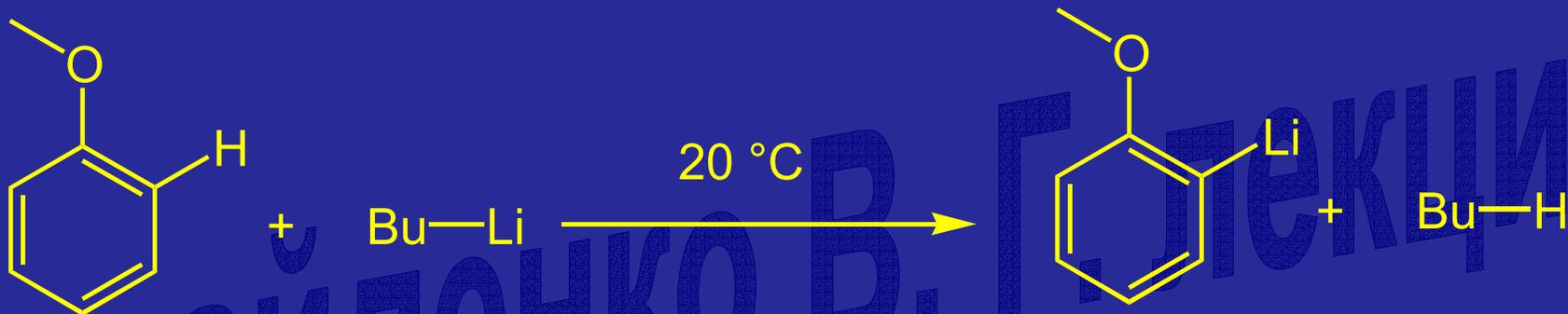


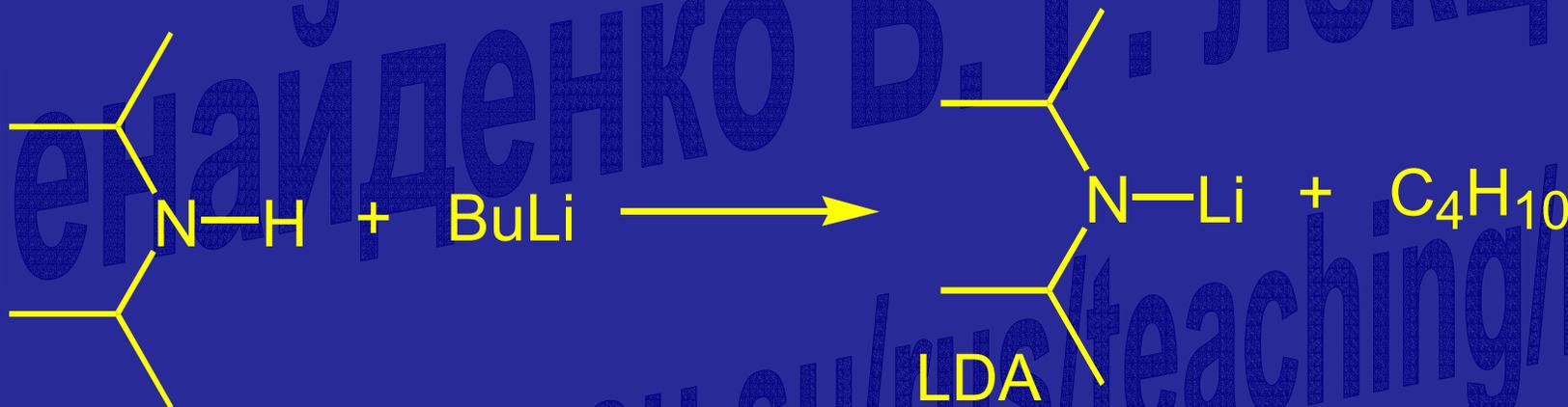
Металлорганические соединения - супероснования



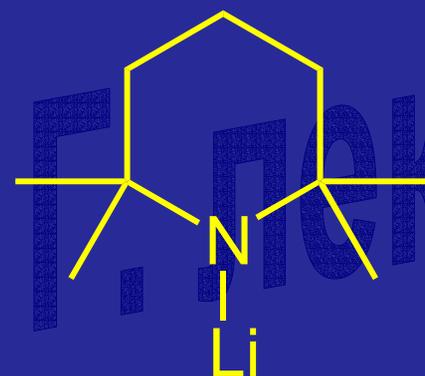
Реакция металлирования



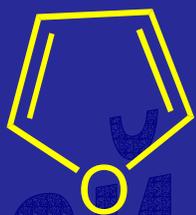




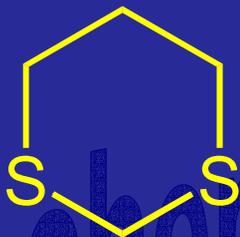
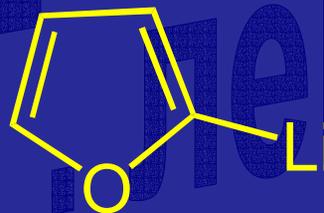
M = Li, Na, K



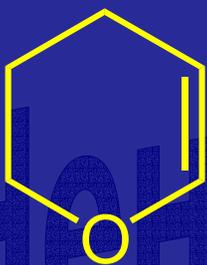
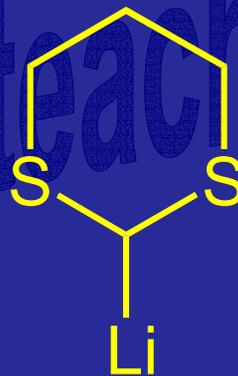
LTMP



+



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TMEDA

