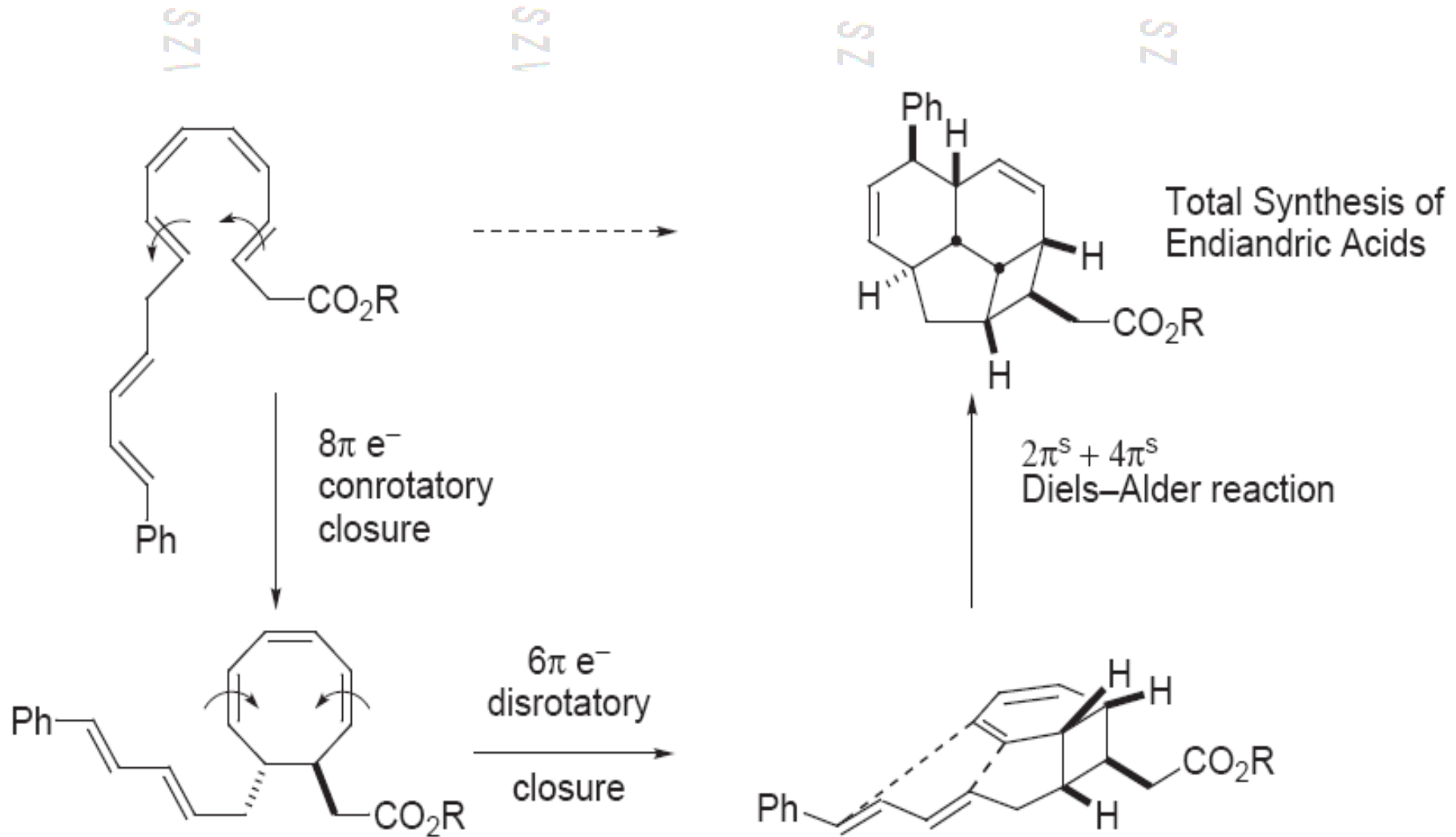


5. Перициклические реакции

- Классификация, механизмы, определения
- Правила Вудворда-Хоффмана
- Реакции циклоприсоединения – (2+1): карбены/бораны; (2+2): Нойори, кетены, фото, еноны; (4+2): циклопентаны через [3+2], циклогексаны через [4+2]
- Реакция Дильса-Альдера: диены и диенофилы, региохимия, стереохимия, катализ
- Электроциклические реакции: примеры, стереохимия, сравнение термо- и фото, Назаров

- Для начала...

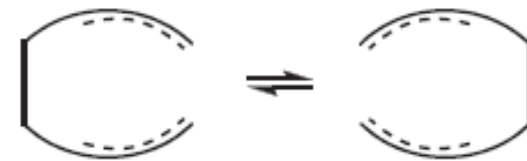
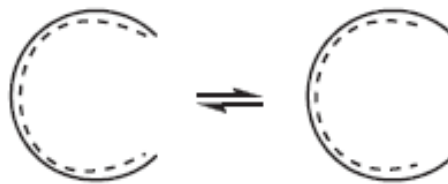
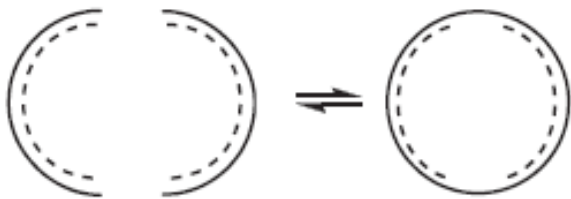


Nicolaou *J. Am. Chem. Soc.* **1982**, *104*, 5555, 5557, 5558 and 5560.

- Определения

Перициклические реакции:

Реакции, протекающие через *циклическое* переходное состояние с согласованным передвижением электронов и одновременным образованием и разрывом связей

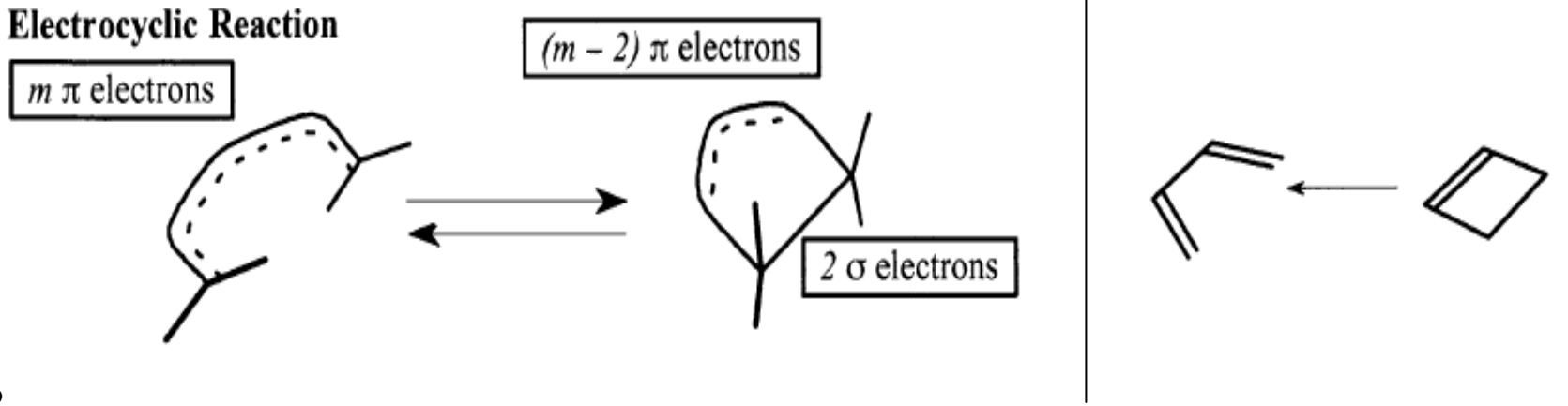
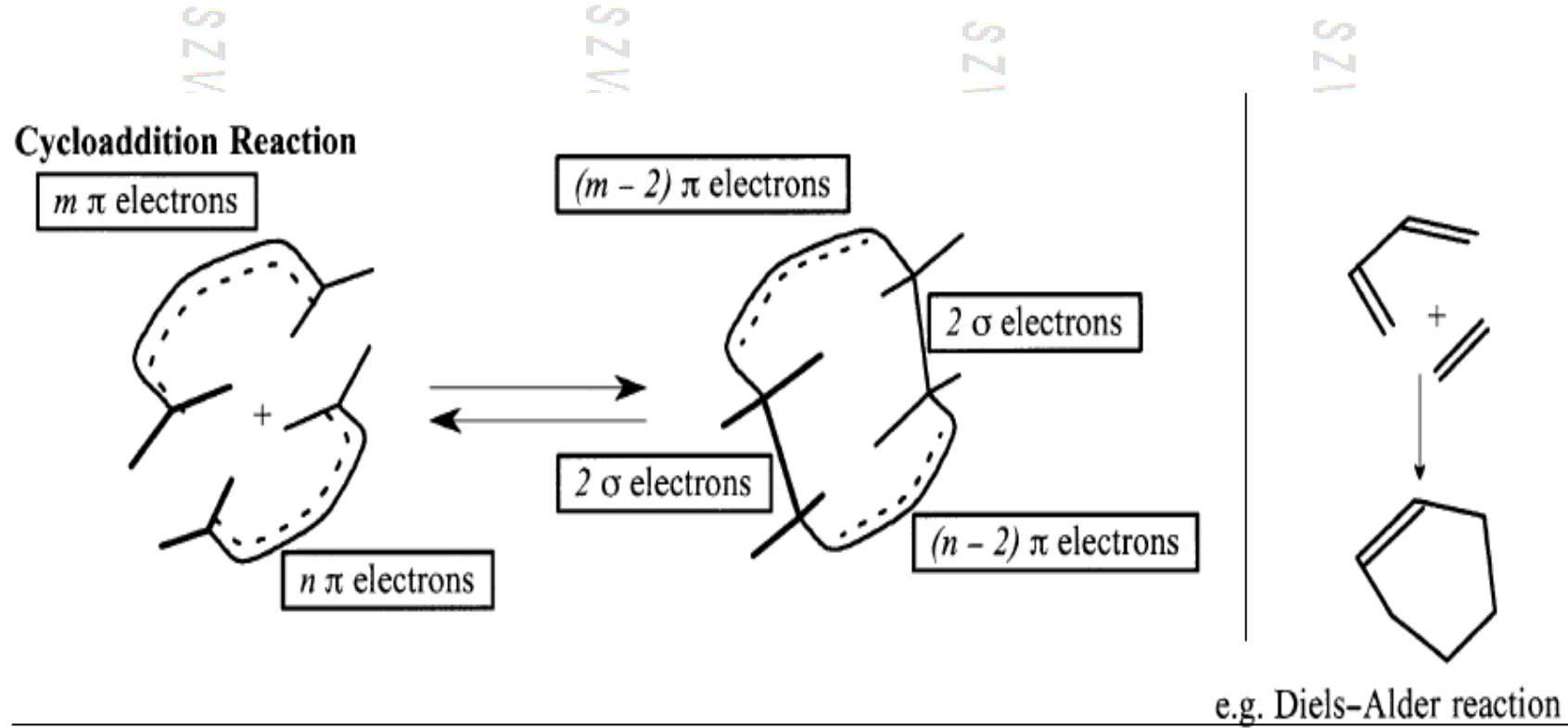


Циклоприсоединение

Электроциклические

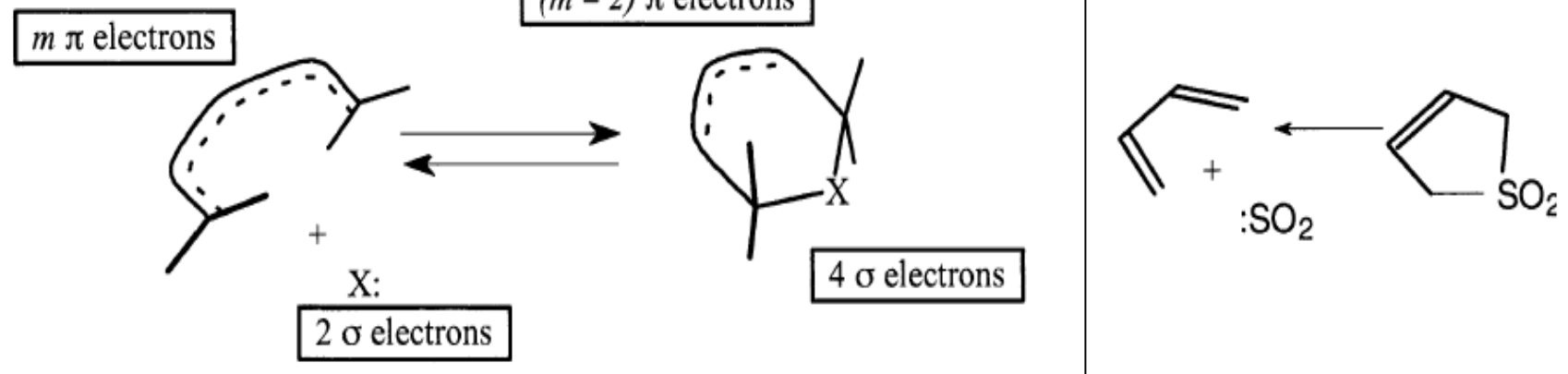
Сигматропные перегруппировки

• Классификация

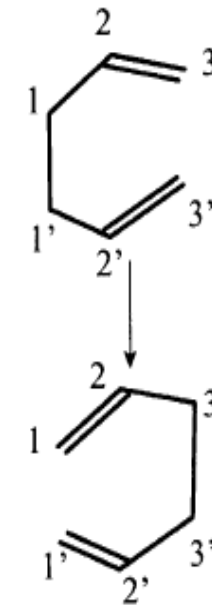
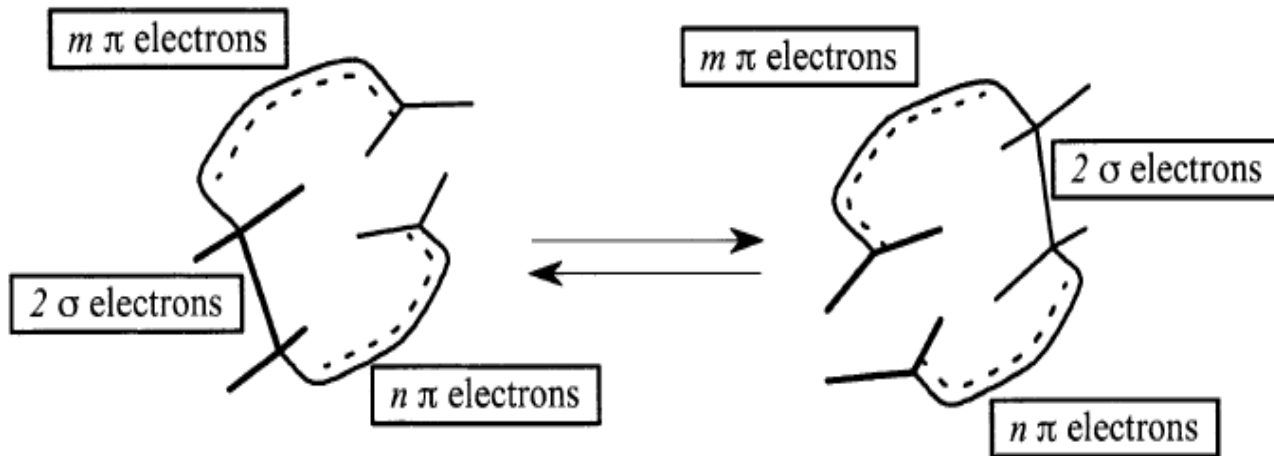


• Классификация

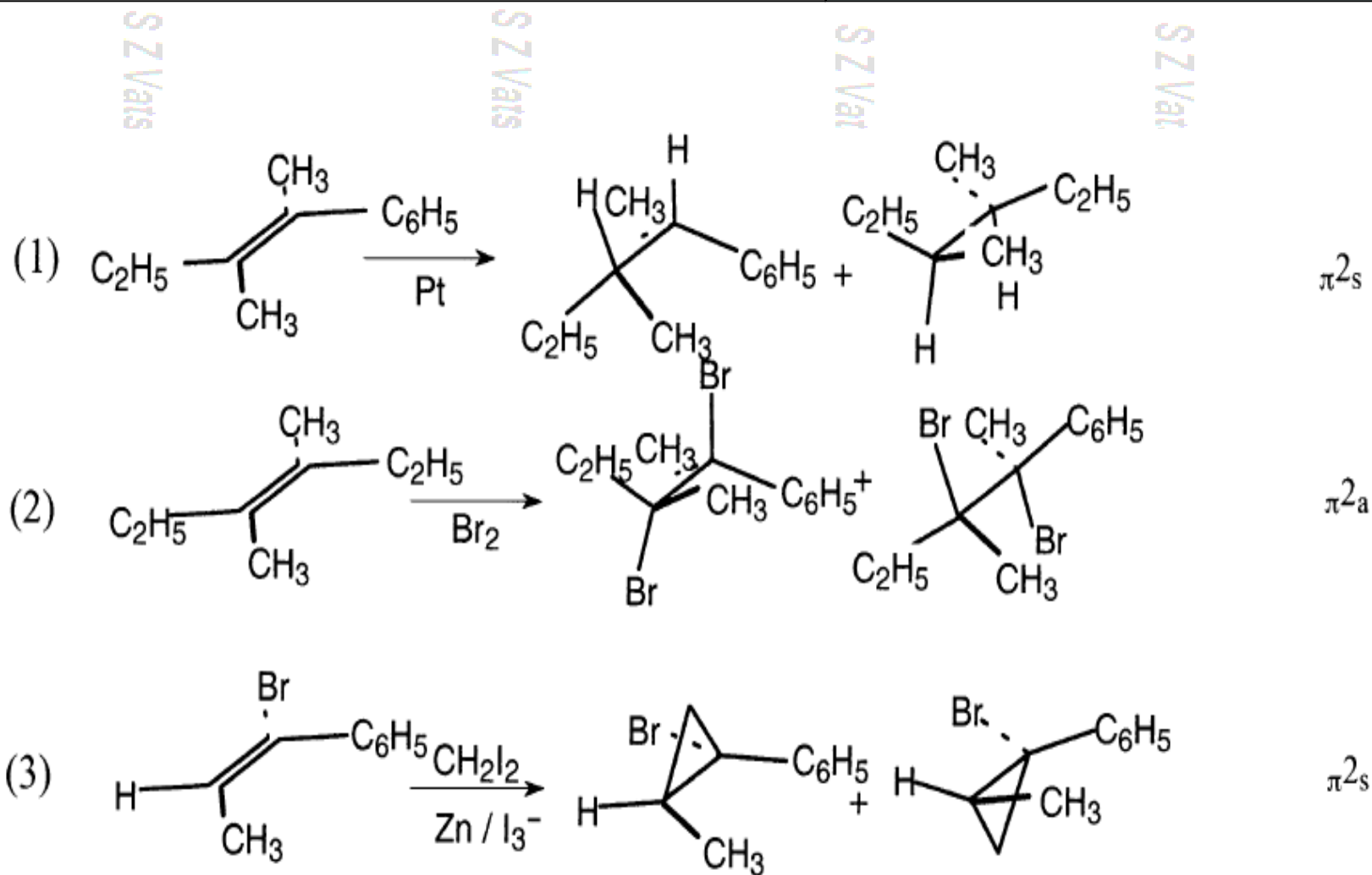
Cheletropic Reaction



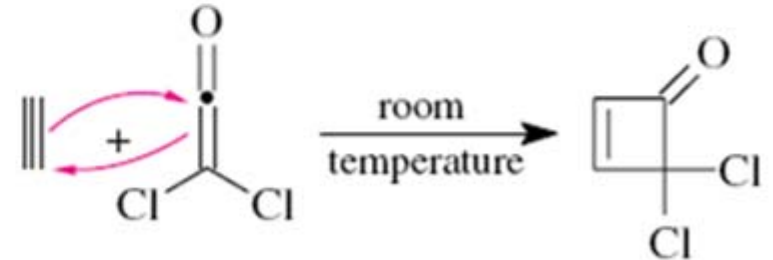
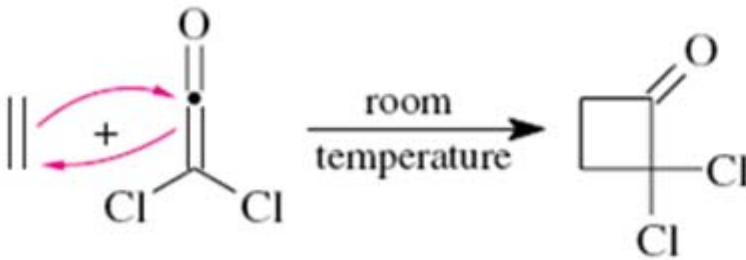
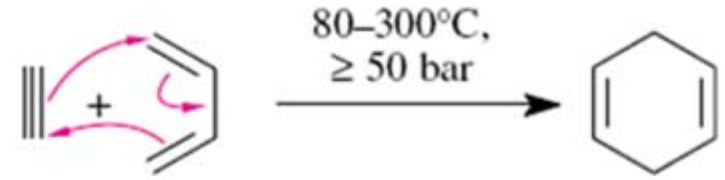
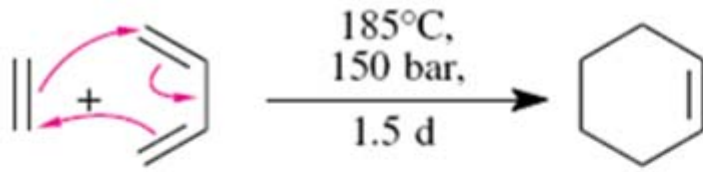
Sigmatropic Rearrangement



e.g. Cope rearrangement



Примеры реакций – как объяснить

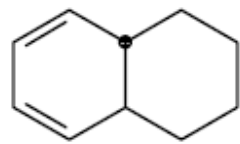


e's lectures

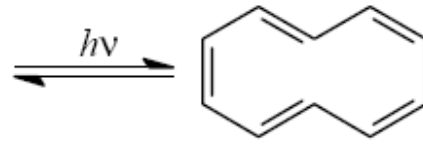
e's/e

e's/e

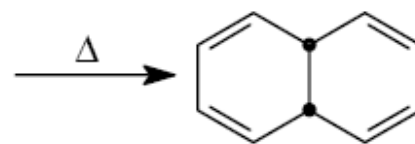
e's/e



транс-9,10-дигидронафталин



циклодекапентаен



цис-9,10-дигидронафталин

• Правила Вудворда-Хоффмана (1965)

Перициклические реакции



Roald Hoffman

1981

for their theories, developed independently, concerning the course of chemical reactions.



Robert B. Woodward

1965

for his outstanding achievements in the art of organic synthesis.

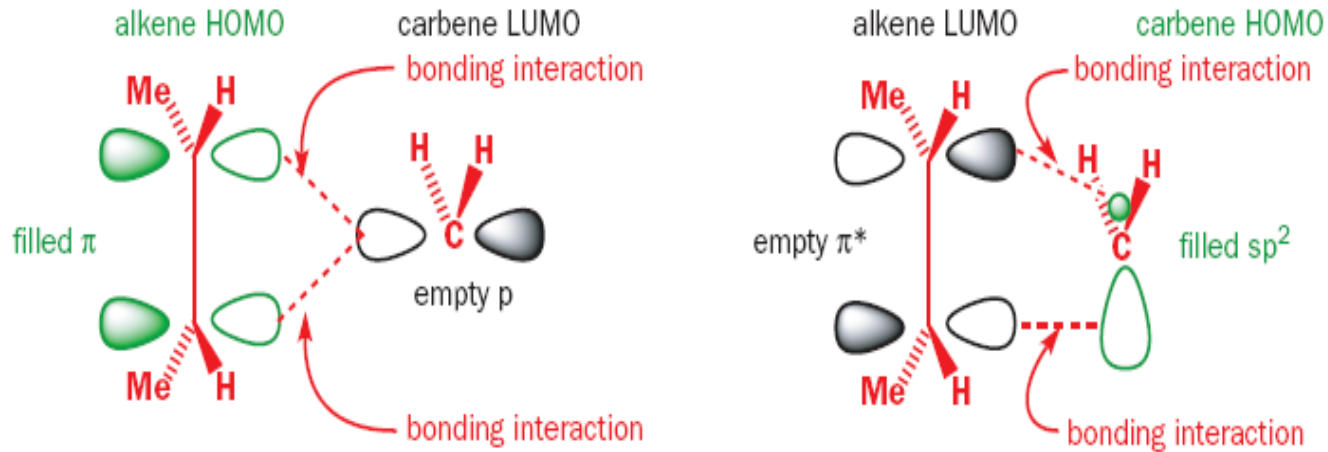


Термическая перициклическая реакция разрешена, если количество электронов, вовлеченных в процесс, равно $4n+2$. При этом оба реагента должны реагировать супраповерхностно (или оба антараповерхностно).

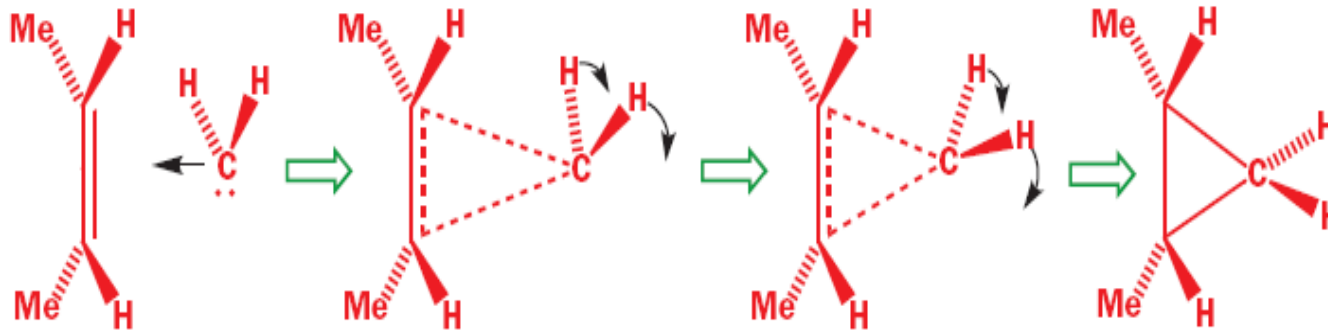
Если количество вовлеченных электронов $4n$, то реакция разрешена термически, если один из реагентов реагирует супраповерхностно, а второй -

- (2+1): циклопропанирование

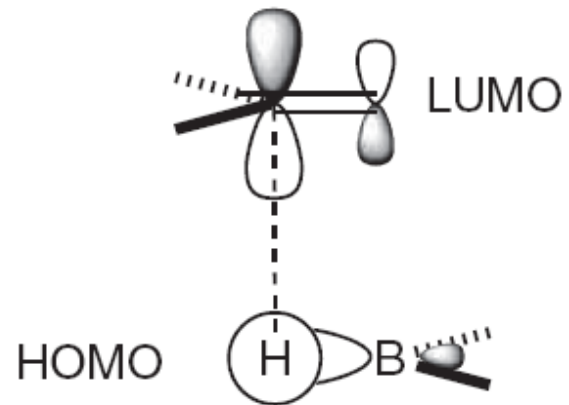
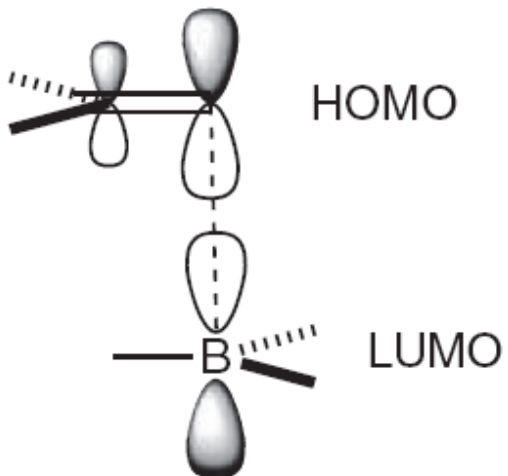
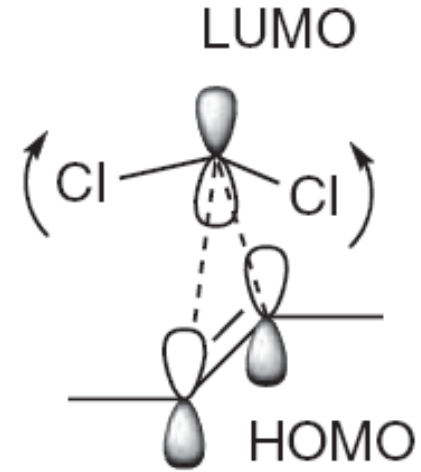
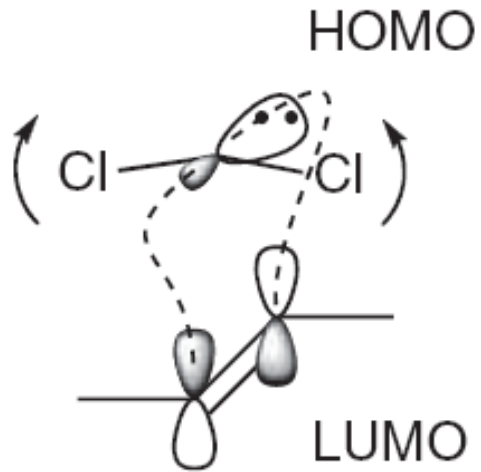
Циклопропанирование



'docking' of the carbene on to the alkene



• Карбены и бораны



• (2π+2π): реакция Нойори

1ZS

1ZS

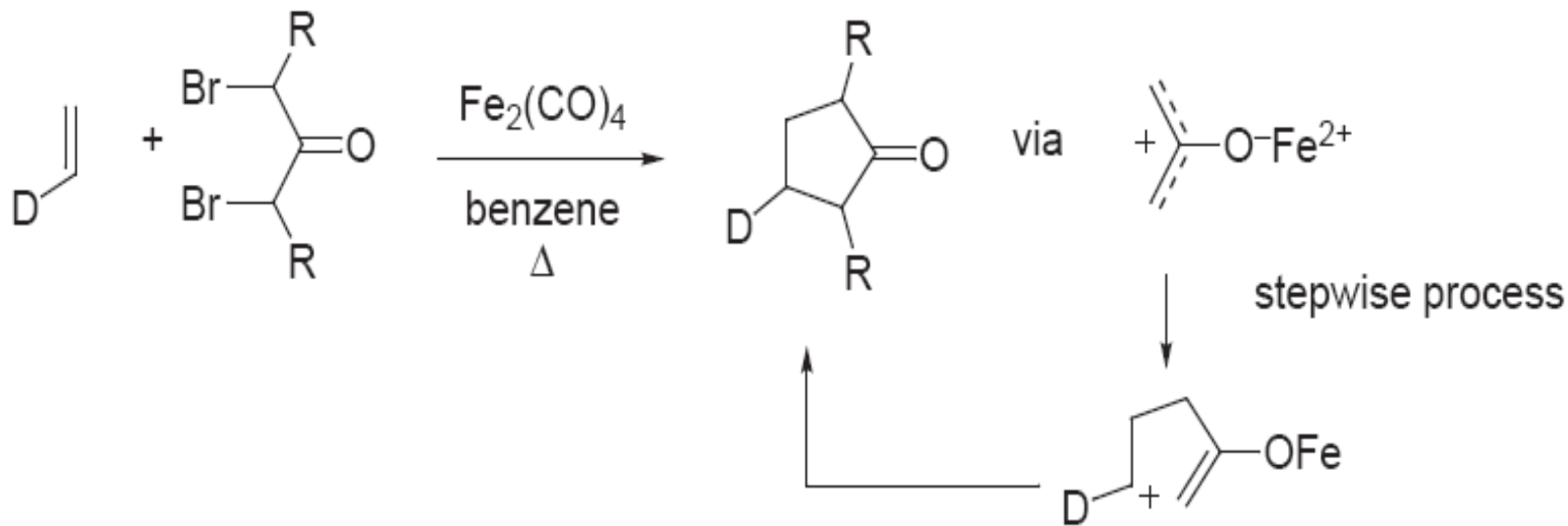
1ZS

1ZS

1. (2π + 2π)



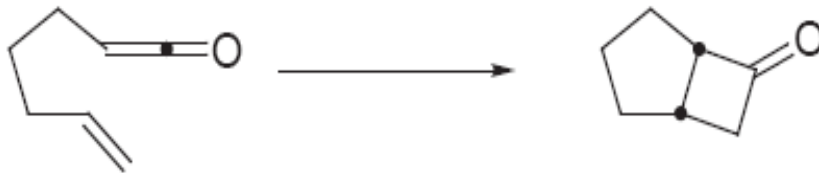
- Noyori reaction: *J. Am. Chem. Soc.* **1972**, *94*, 1772.
- J. Am. Chem. Soc.* **1973**, *95*, 2722.
- J. Am. Chem. Soc.* **1977**, *99*, 5196.
- J. Am. Chem. Soc.* **1978**, *100*, 1793.



- (2π+2π): кетены

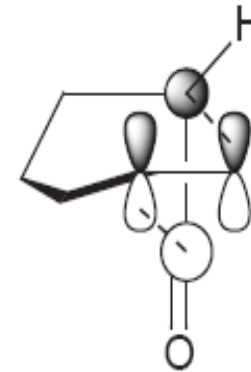
S Z Varsadz

Org. React. 1995, 45, 159.



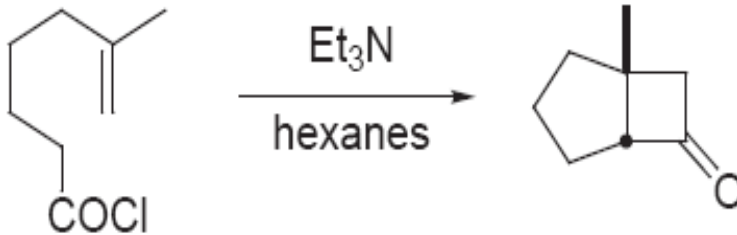
S Z Varsadz

S Z Varsadz



S Z Varsadz

$2\pi^s + 2\pi^a$
Cycloaddition



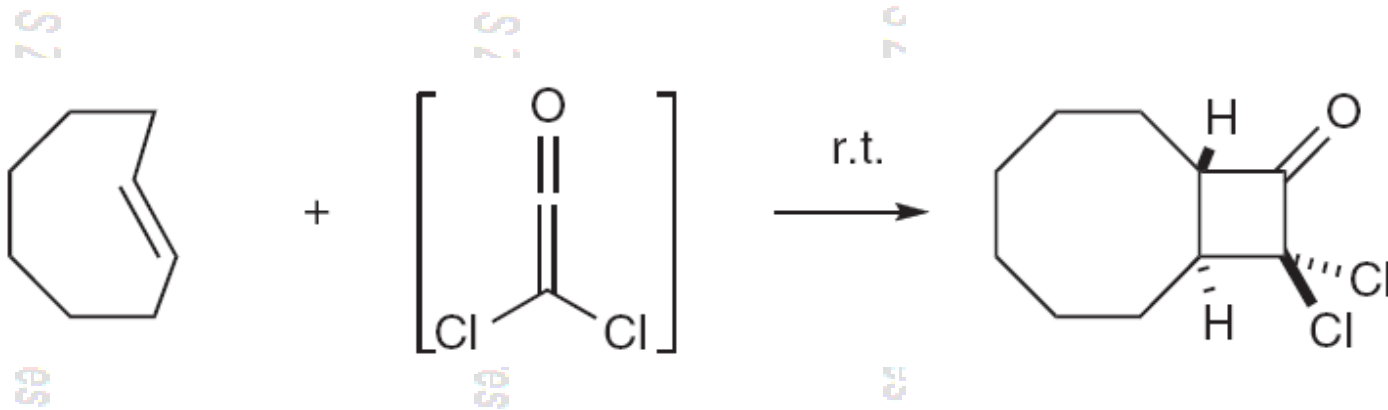
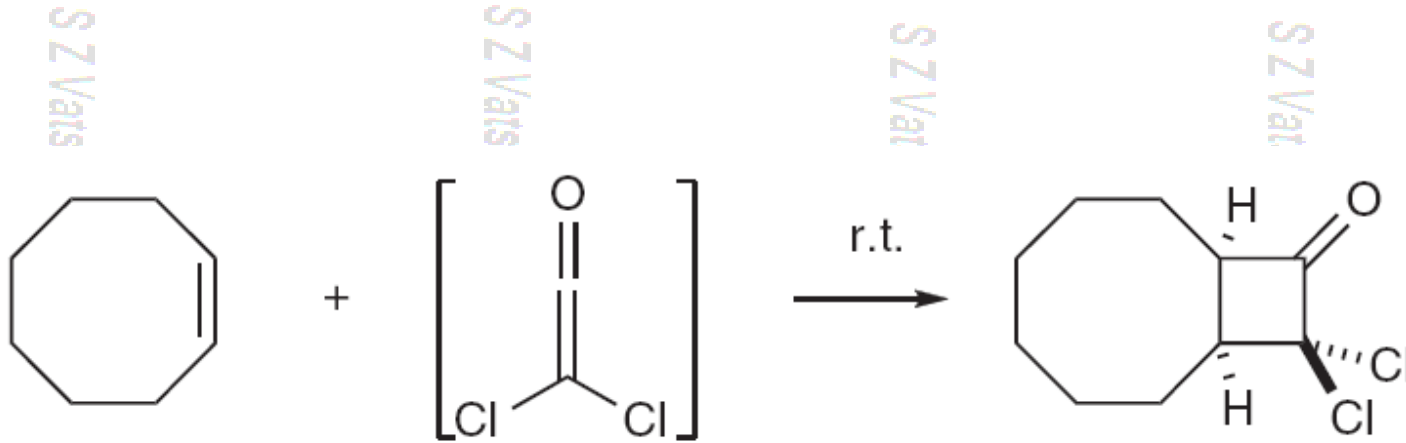
Baldwin J. Chem. Soc., Chem. Commun. 1972, 1337.

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- (2π+2π): кетены



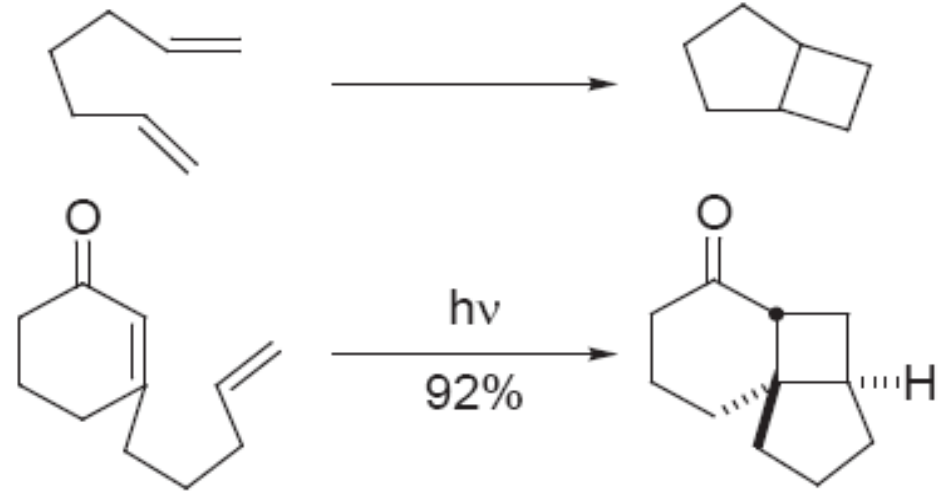
- (2π+2π): алкены, еноны

S Z Vatsadze's lectures

S Z Vatsadze's

S Z Vatsadze

S Z Vatsadze's lectures



Cargill *Tetrahedron Lett.* 1978, 4465.

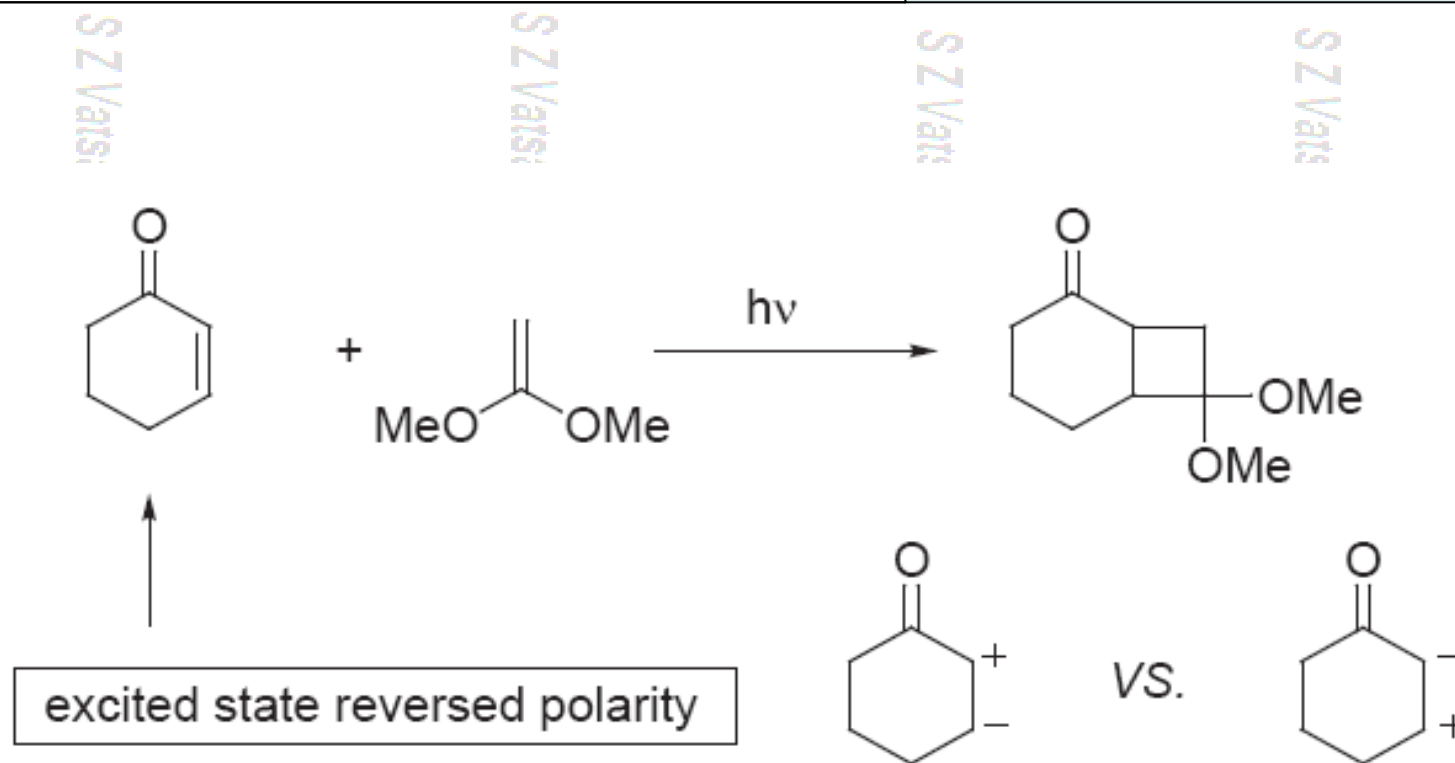
S Z Vatsadze's lectures

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S Z Vatsadze's lectures

- (2π+2π): еноны



Corey J. Am. Chem. Soc. 1964, 86, 5570.

Vres

Vres

Vres

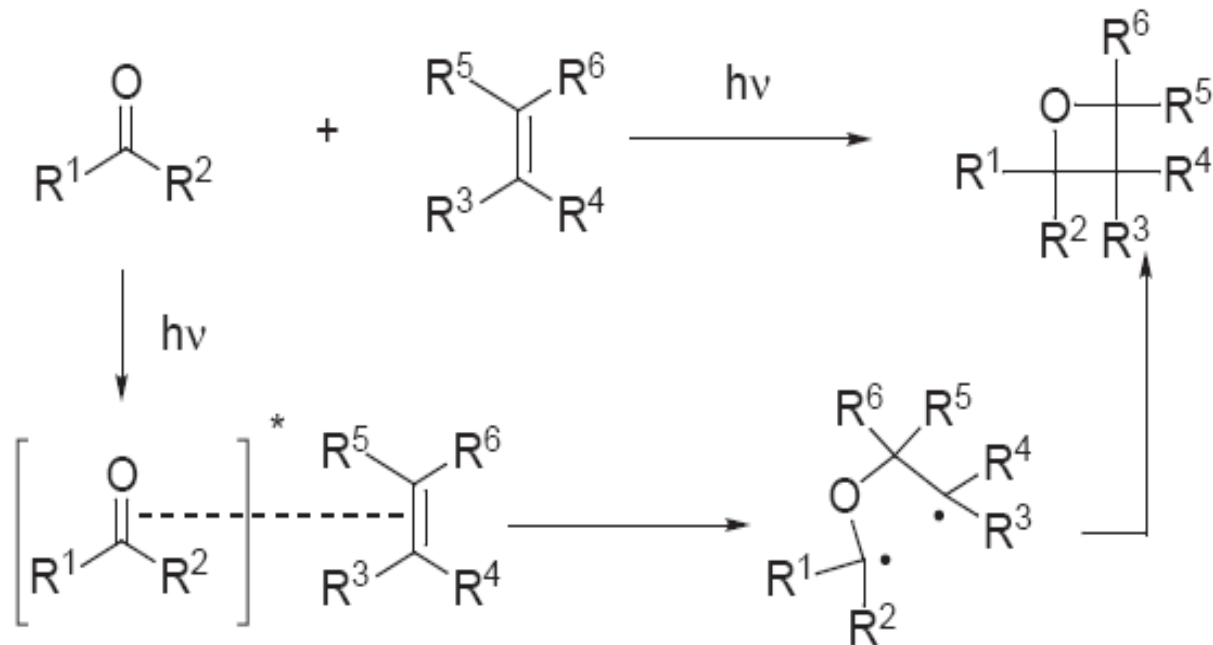
Vres

- (2π+2π): реакция Патерно-Бюхи

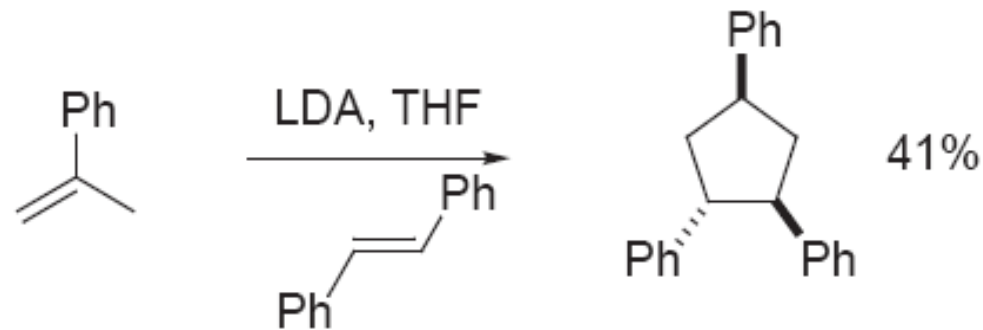
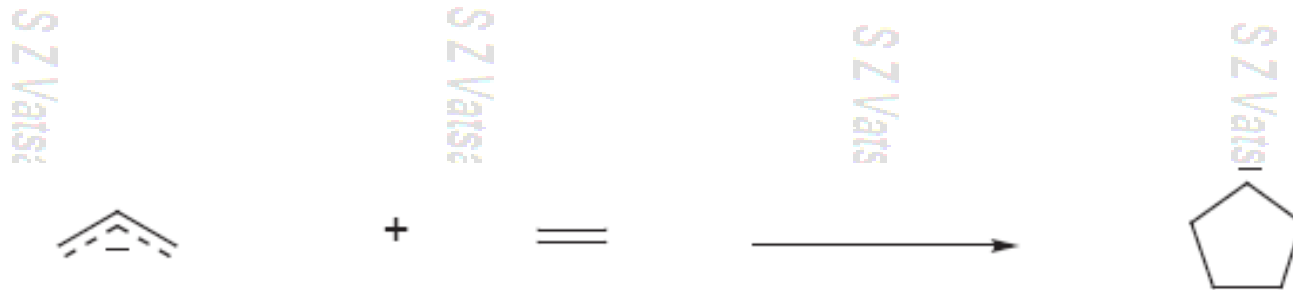
Comprehensive Org. Syn., Vol. 5, 151.

Dermuth Synthesis 1989, 152.

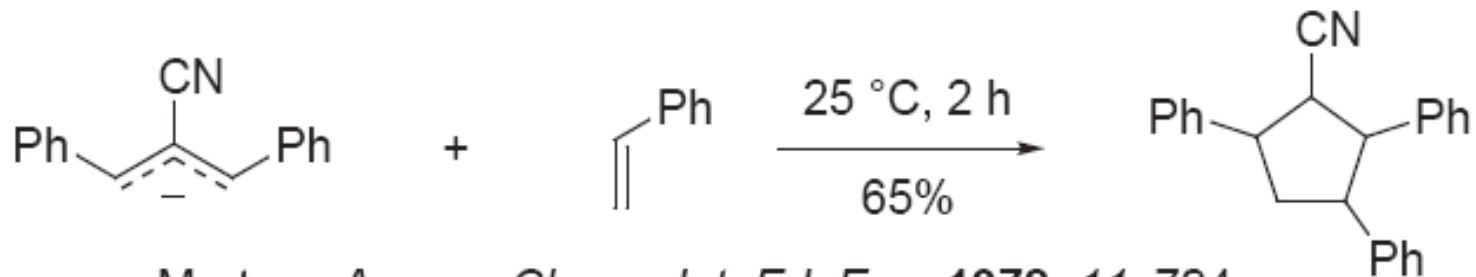
First studied in detail by Buchi *J. Am. Chem. Soc.* 1954, 76, 4327.



- (4π+2π) или [3+2]

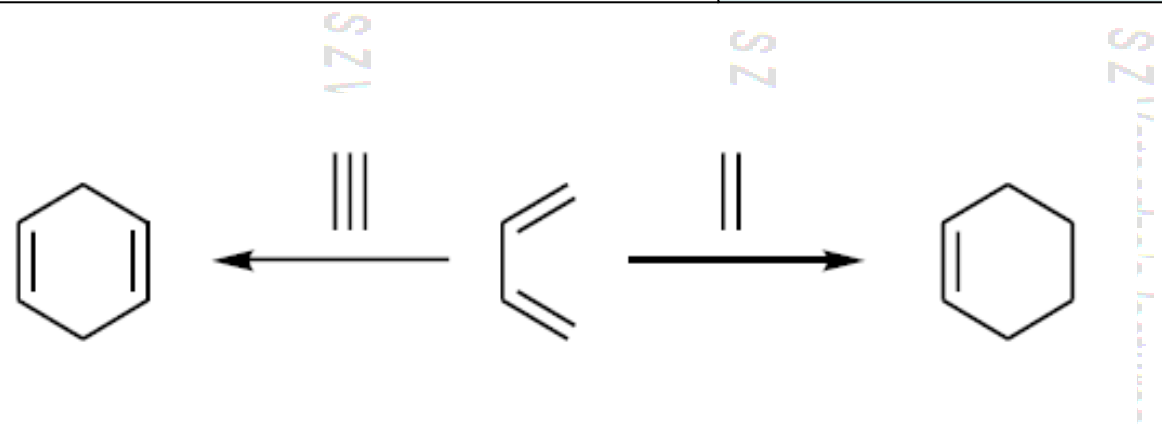


Kauffman *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 292.

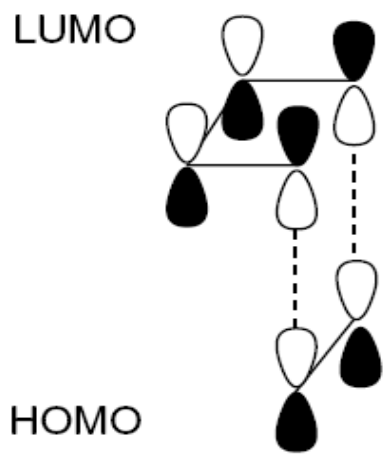


Martens *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 724.

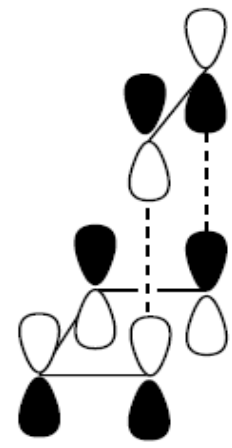
S Z Vatsadze's lectures



S Z Vatsadze's lectures



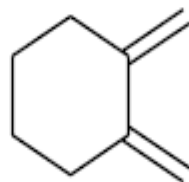
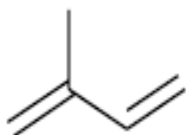
inverse



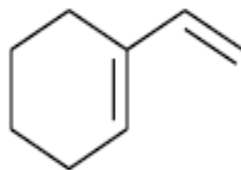
normal

• Диены

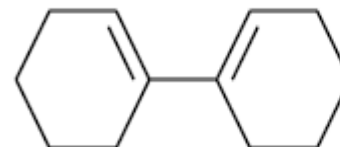
S Z V a t



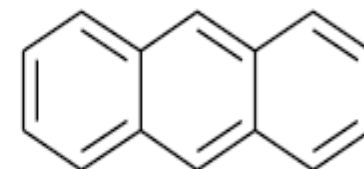
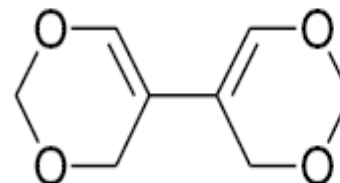
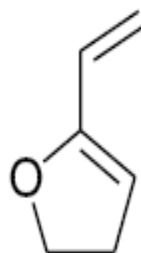
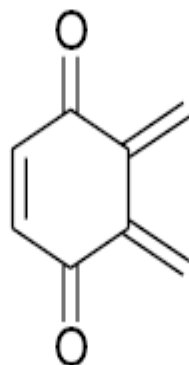
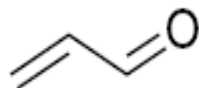
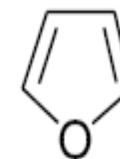
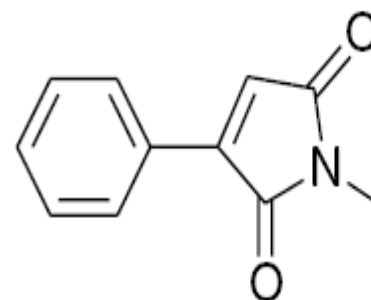
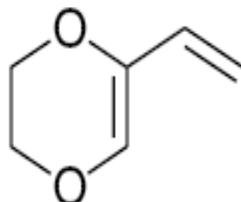
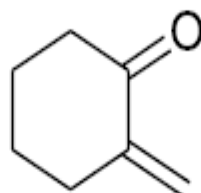
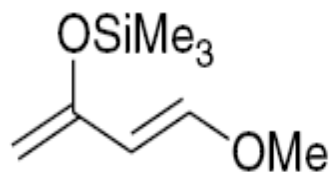
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S Z V a



S Z V a



• Диены

[4+2]-Циклоприсоединение

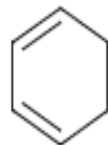
S Z Vatsadze's lectures



S Z Vats



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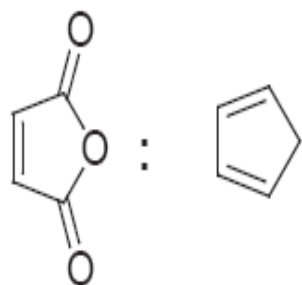
S Z Vats



res

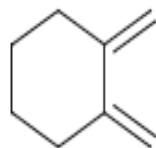


S Z Vatsadze's lectures

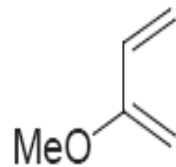


$k_{rel} = 1348$

es

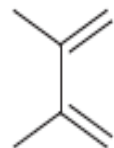


110

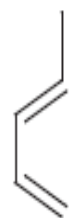


12

es

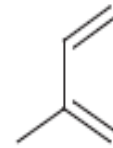


5

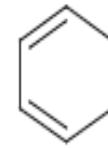


3.3

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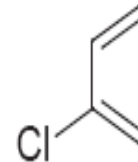
2.2



2



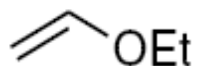
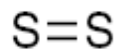
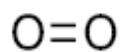
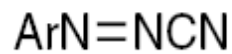
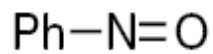
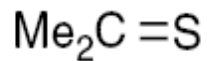
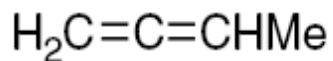
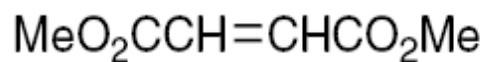
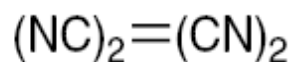
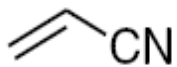
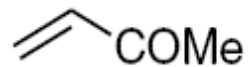
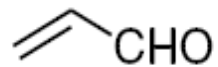
1



0.1

• Диенофилы

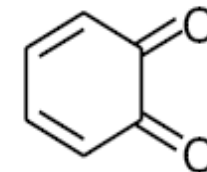
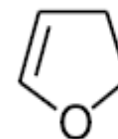
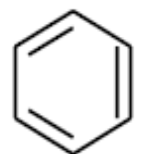
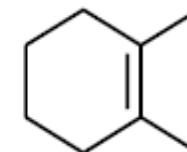
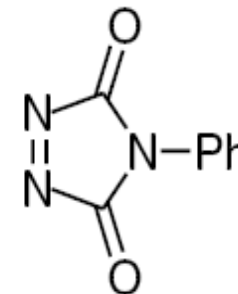
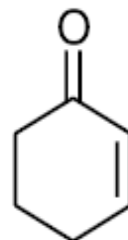
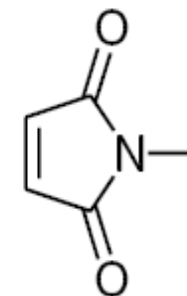
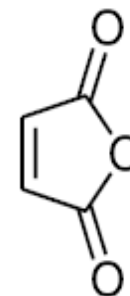
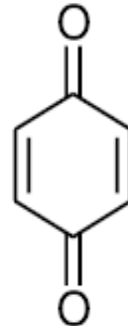
S Z Vais?



S Z Vais?

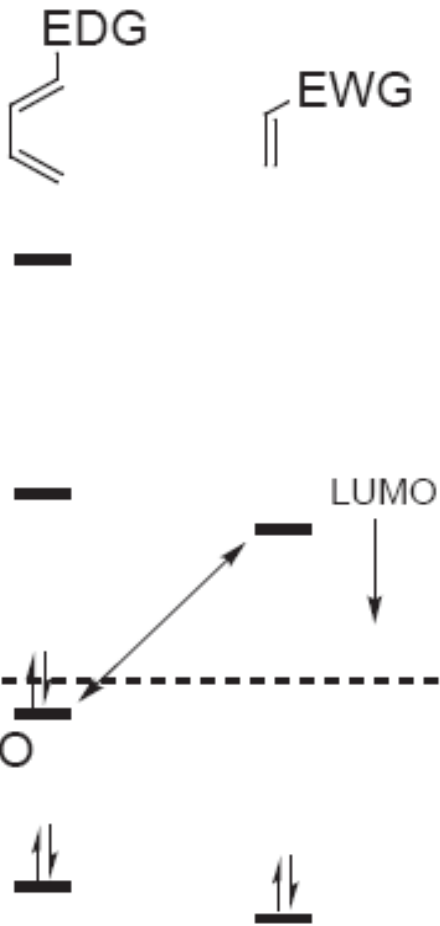
S Z Vais

S Z Vais

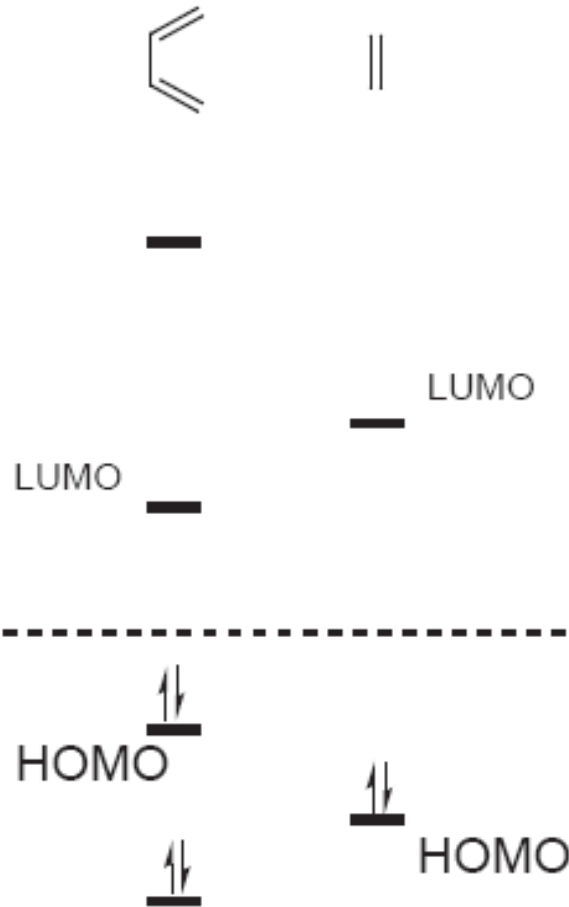


• Орбитальное рассмотрение

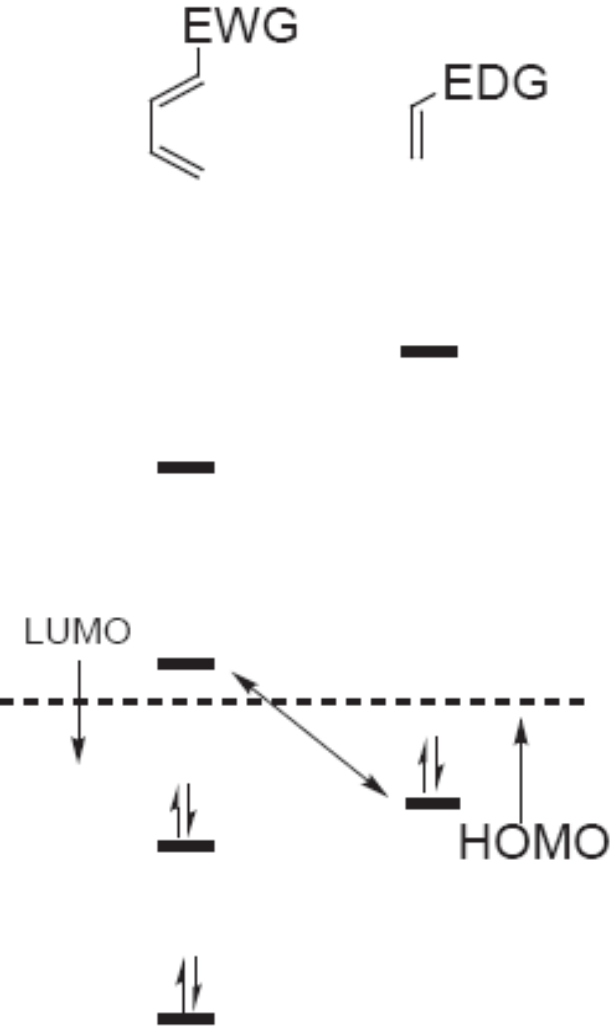
Контроль ВЗМО диена



Обычная



Обратная полярность



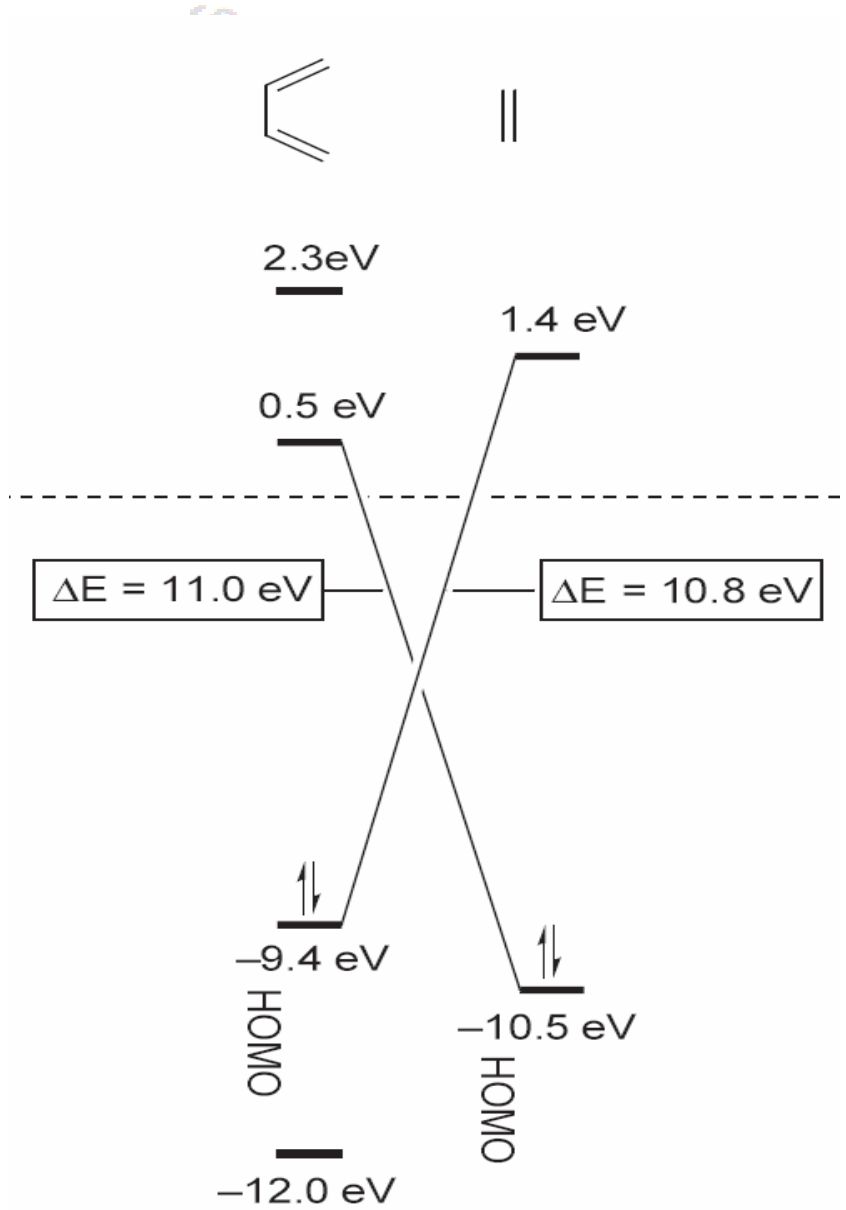
• Орбитальное рассмотрение

S Z Vatsadze's lectures

S Z Vatsadze's lectures

S Z Vatsadze's lectures

S Z Vatsadze's lectures



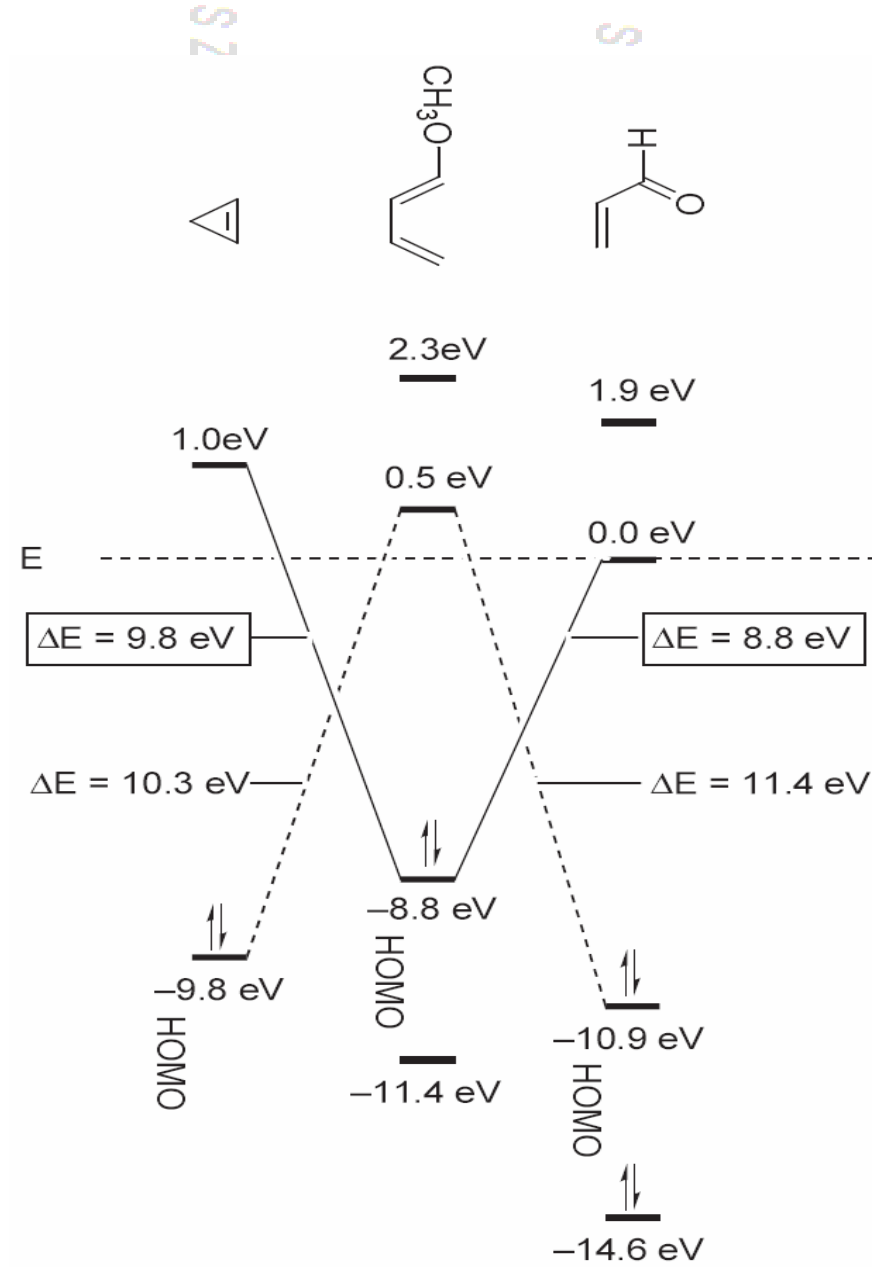
• Орбитальное рассмотрение

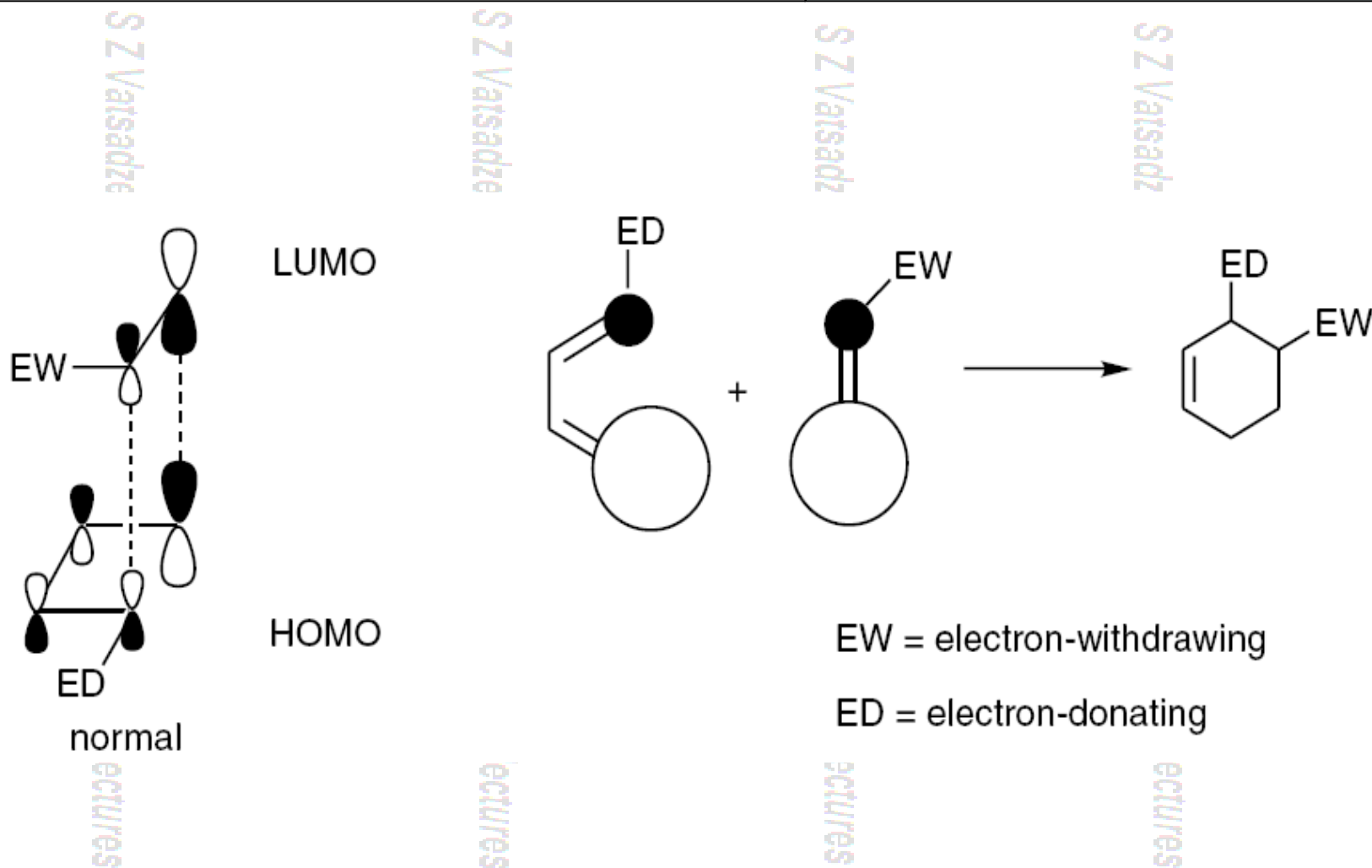
S Z Vatsadze's lectures

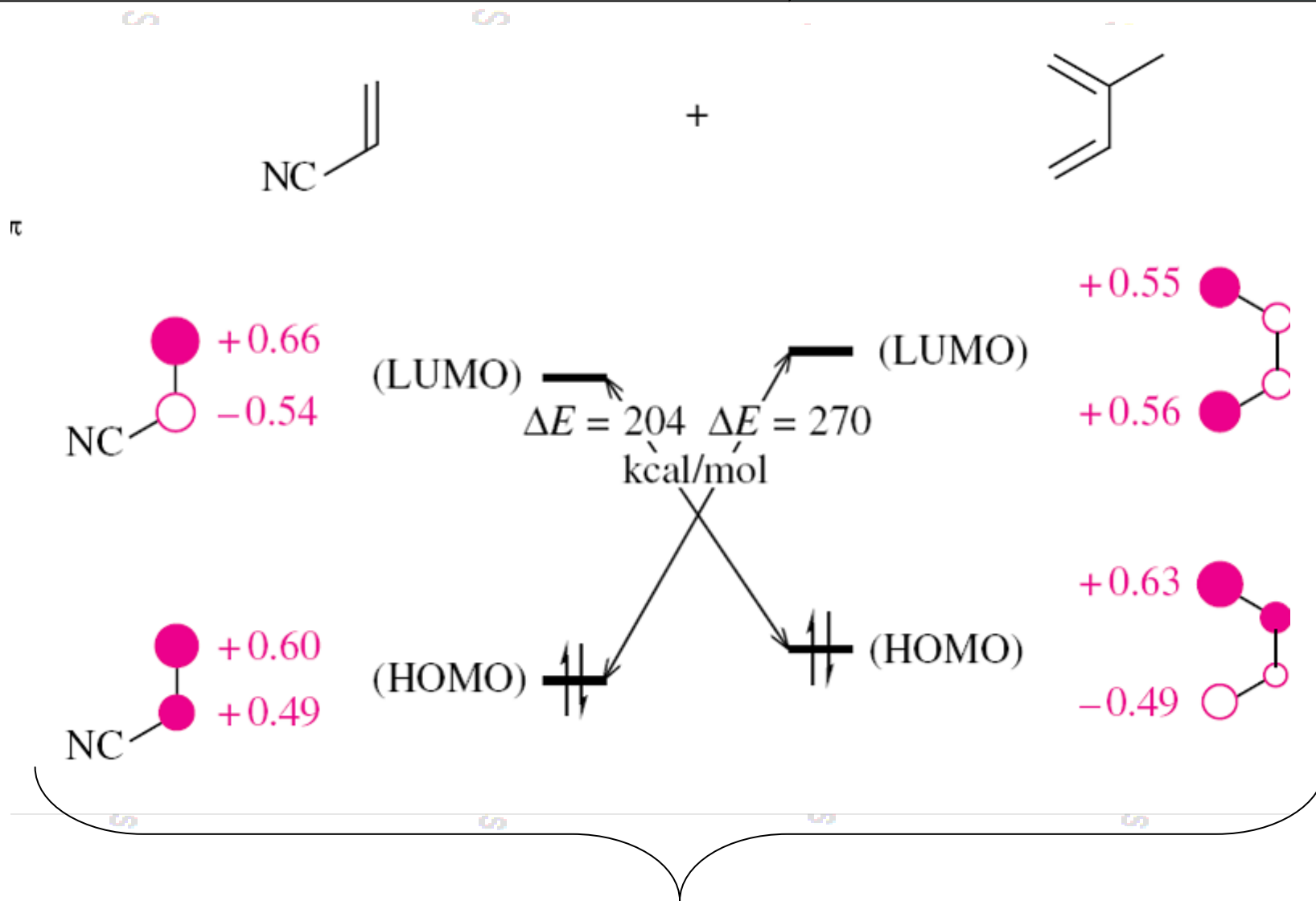
S Z Vatsadze's lectures

S Z Vatsadze's lectures

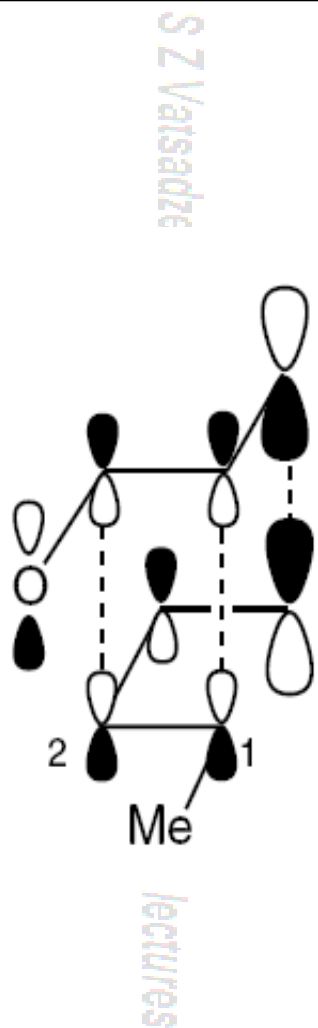
S Z Vatsadze's lectures





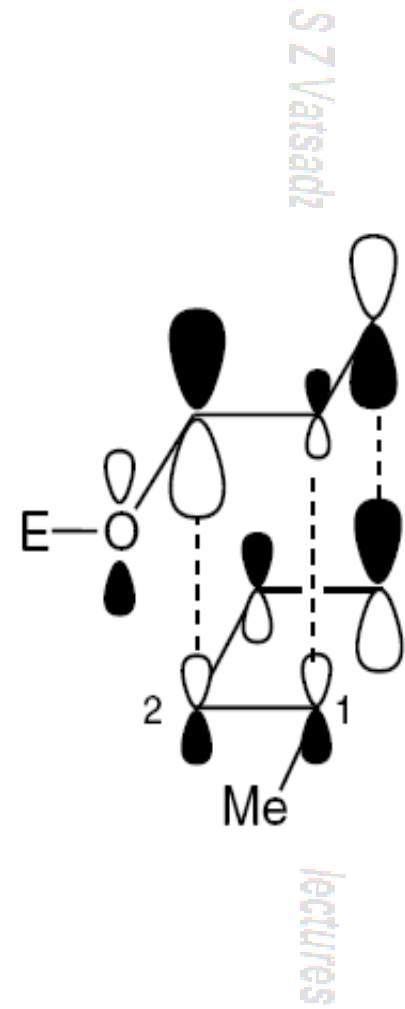


Какой региоизомер более вероятен?



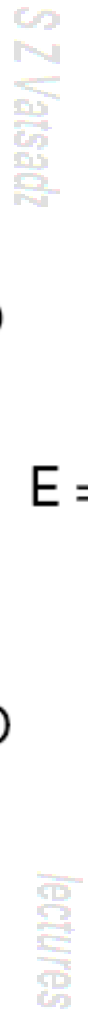
LUMO

HOMO



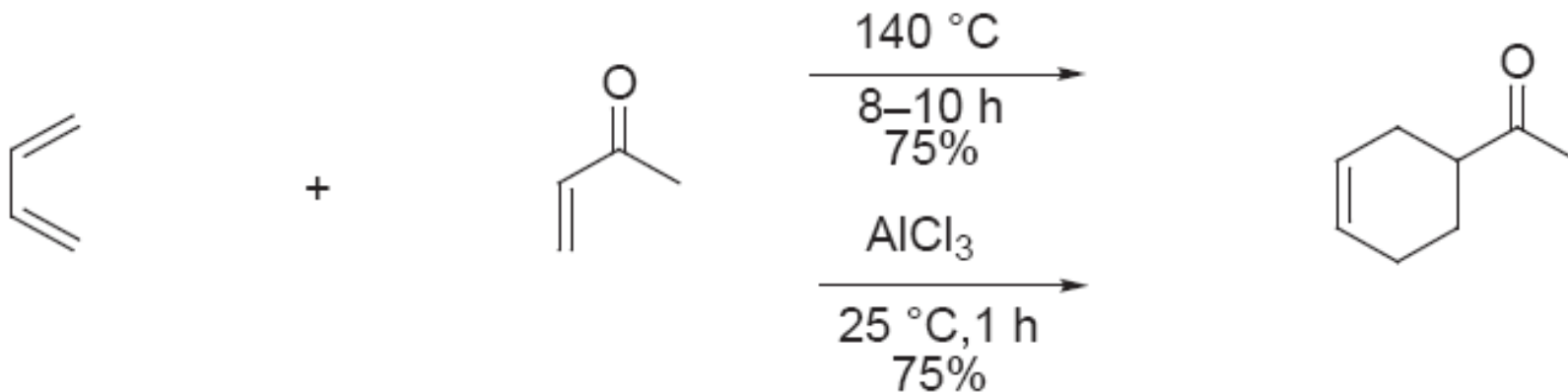
LUMO

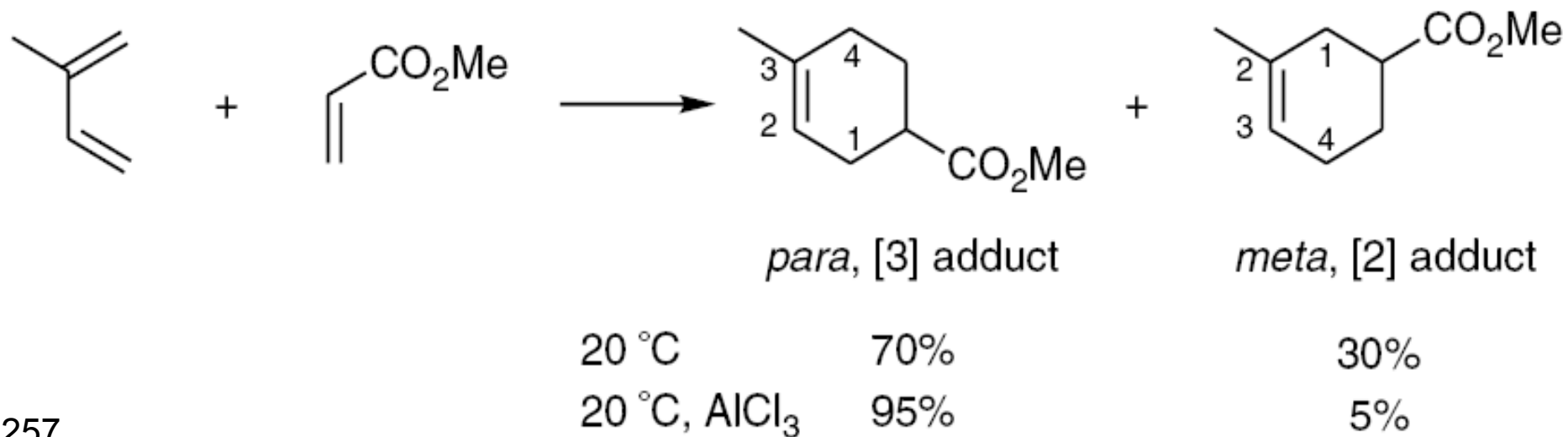
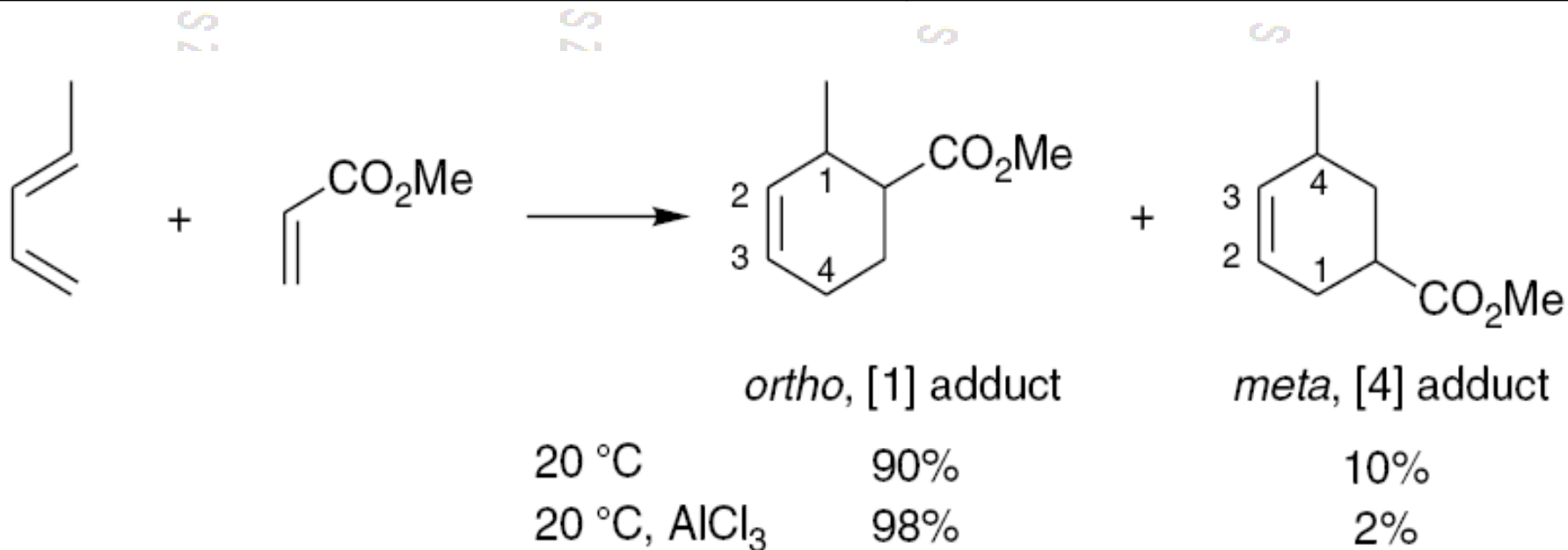
HOMO

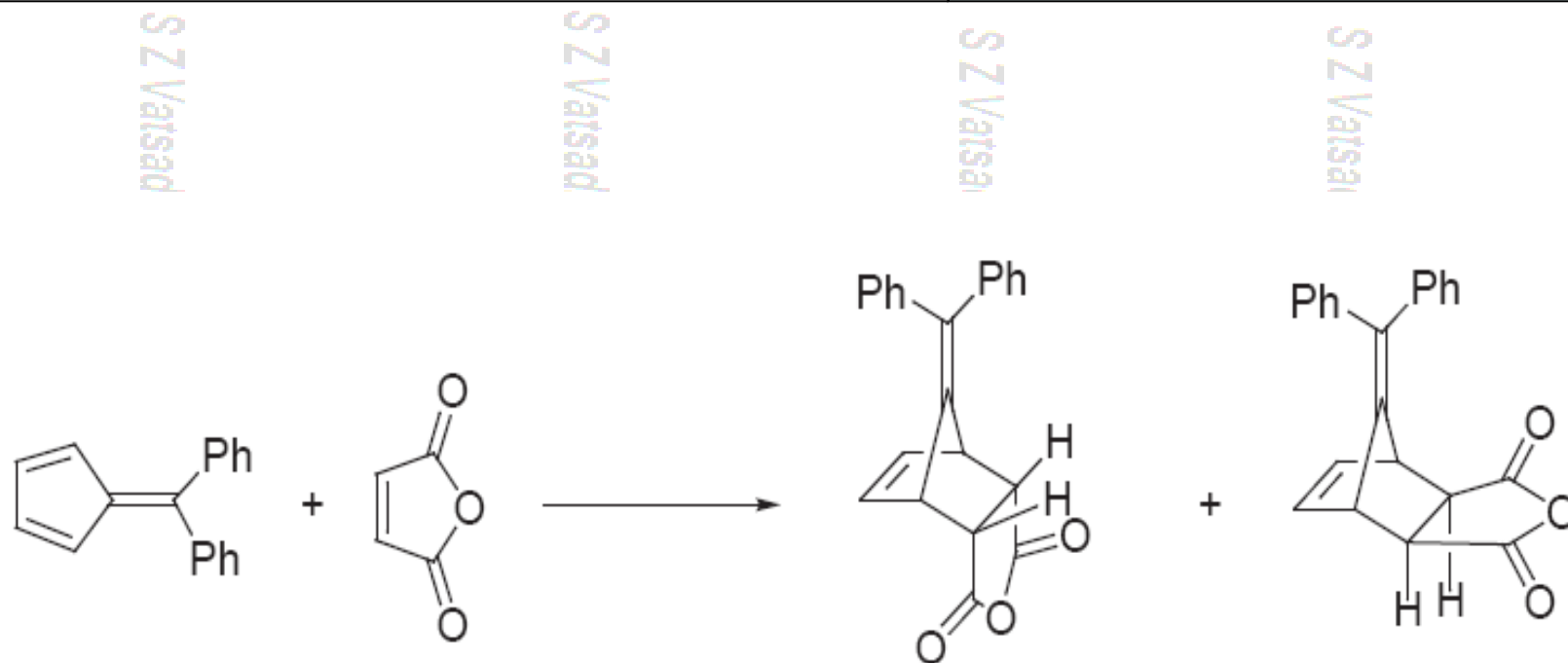


E = Lewis acid

1. Понижение НСМО диенофила – ускорение реакции
2. Увеличение разницы коэффициентов МО диенофила – увеличение региоселективности
3. Изменение коэффициентов МО – изменение вторичных взаимодействий – часто приводит к увеличению *эндо*-селективности







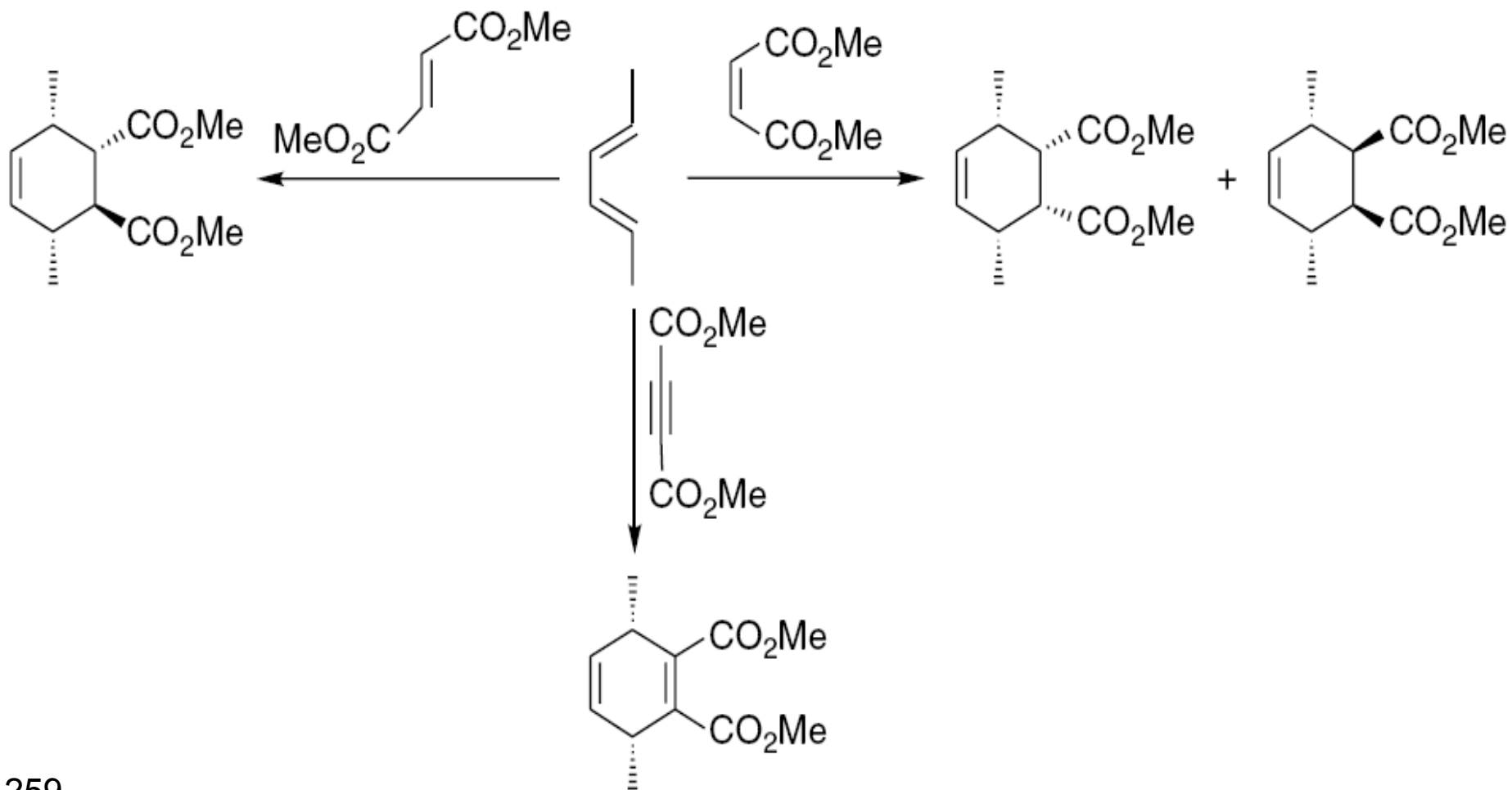
temp.	<i>endo</i>	:	<i>exo</i>
25 °C	100	:	0
140 °C	29	:	71

S Z Vaisadze

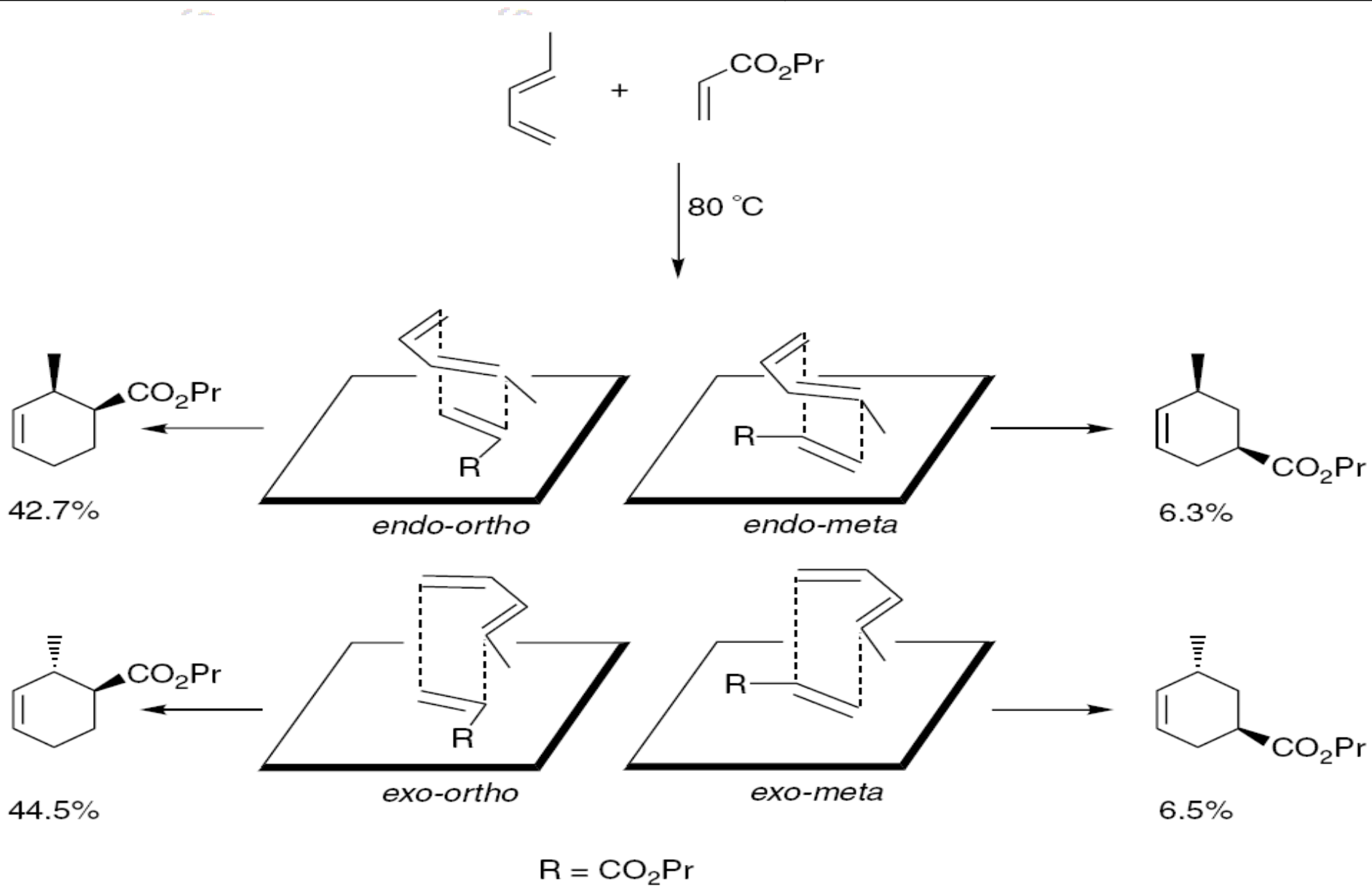
S Z Vaisadze

S Z Vaisadz

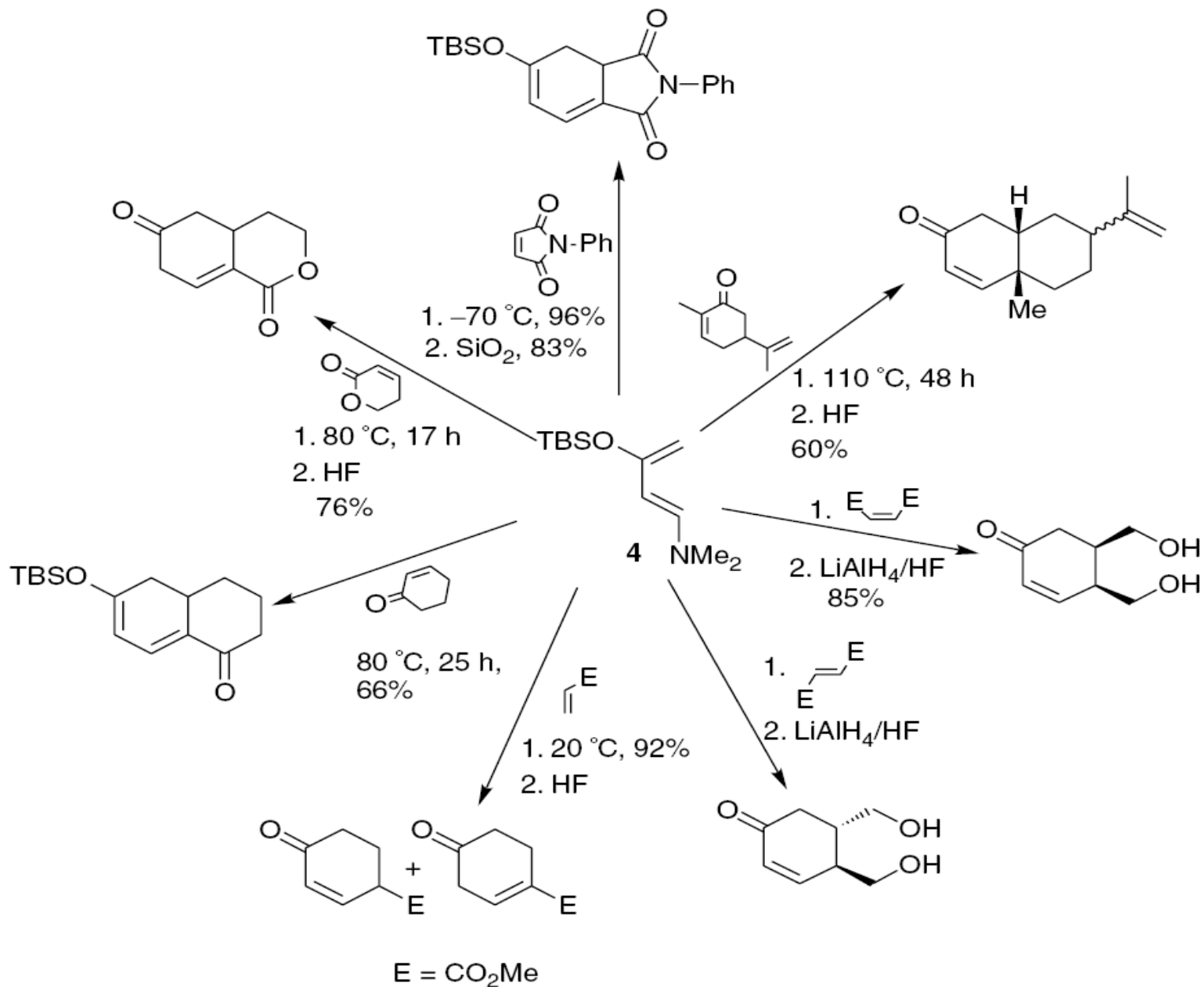
S Z Vaisadz



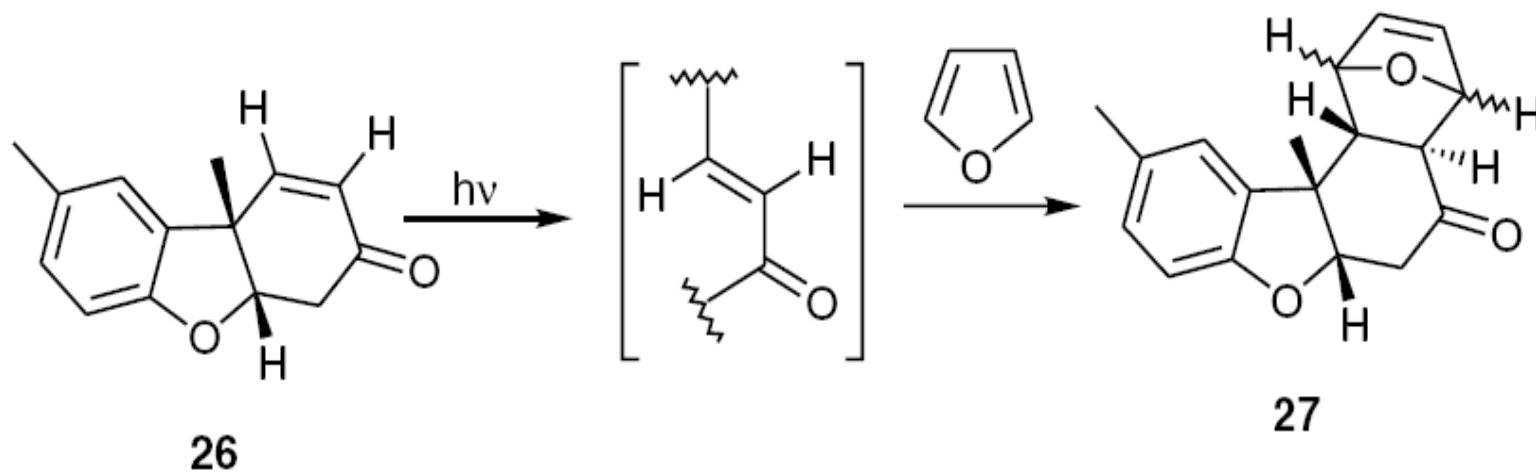
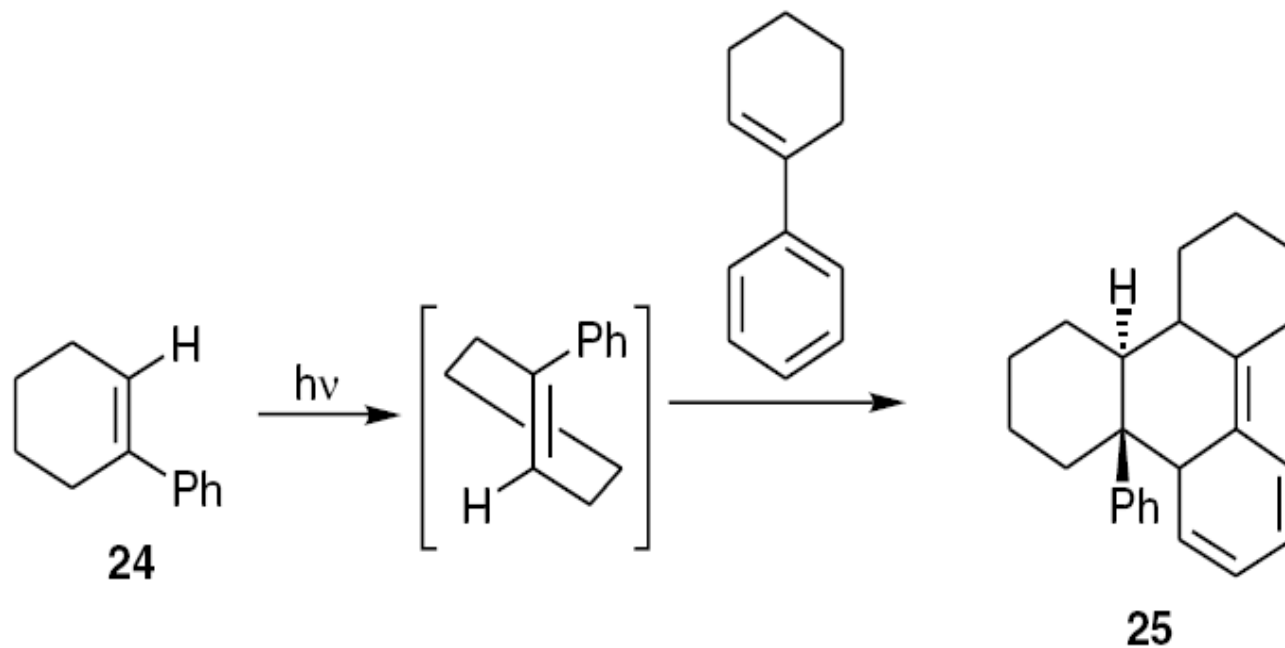
• Стеро + региохимия



Примеры диенов

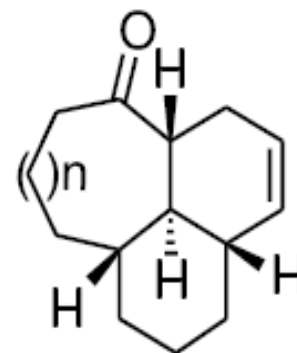
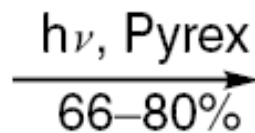
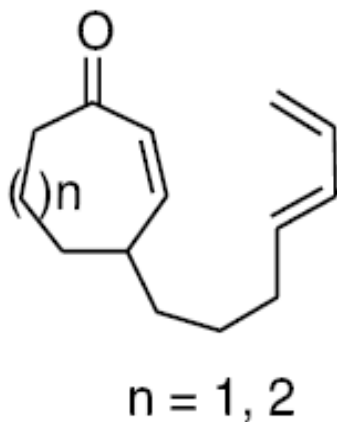


• «Фотохимический» процесс

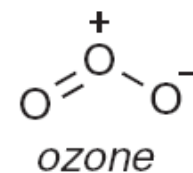
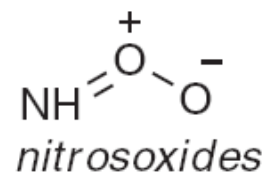
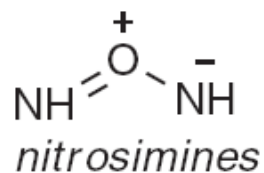
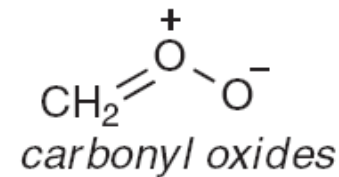
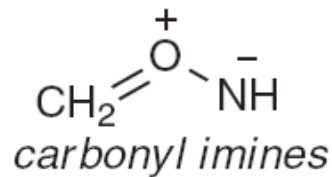
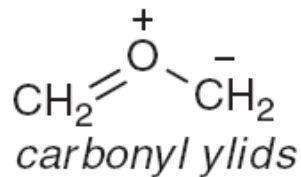
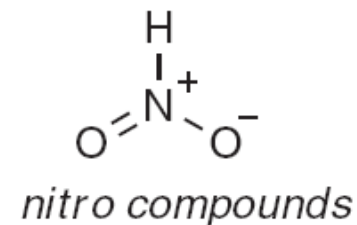
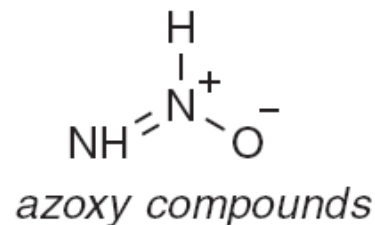
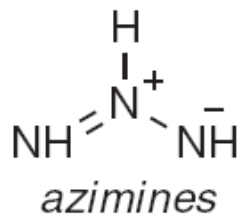
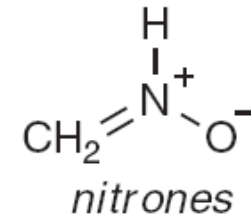
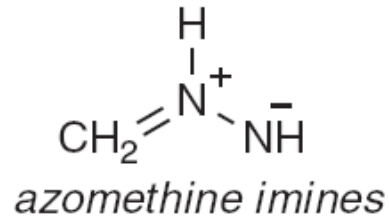
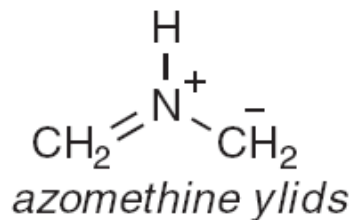
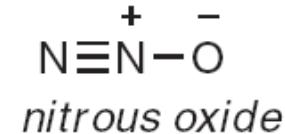
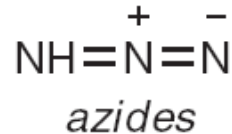
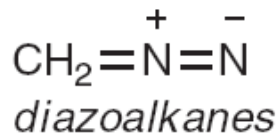
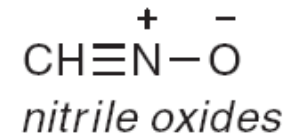
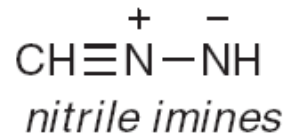
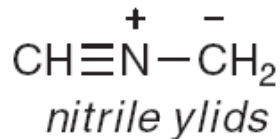


- Избранные примеры

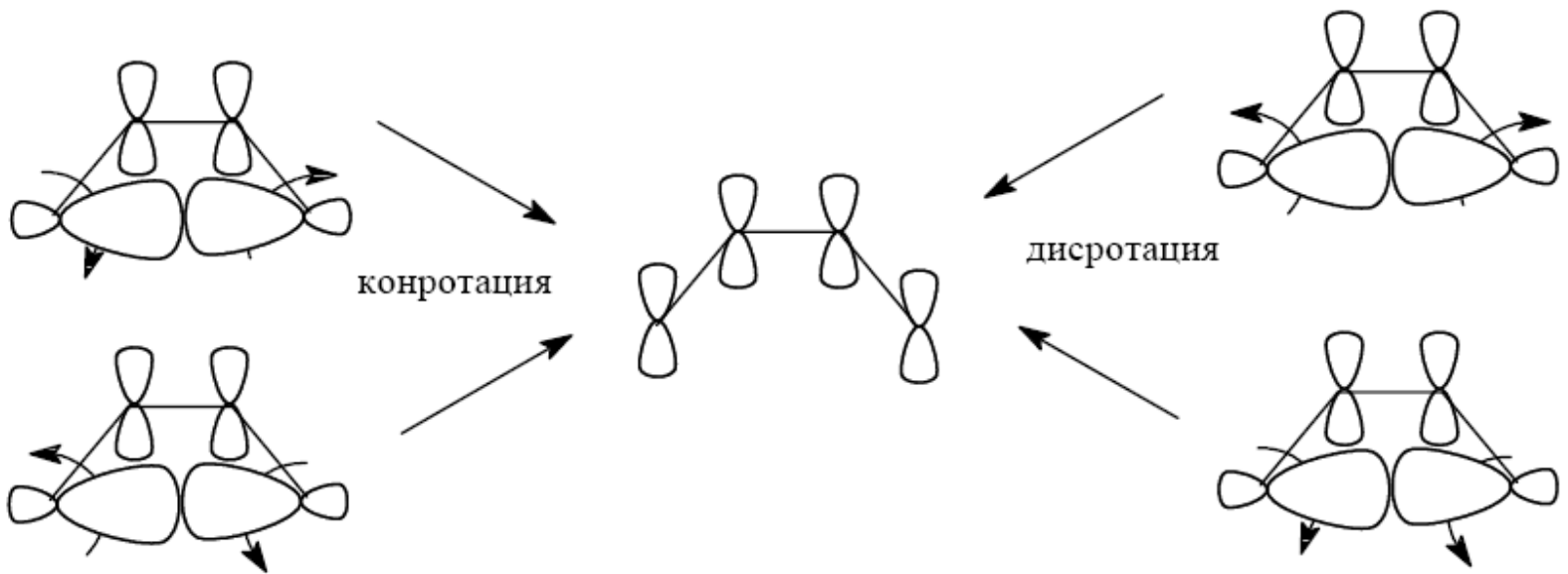
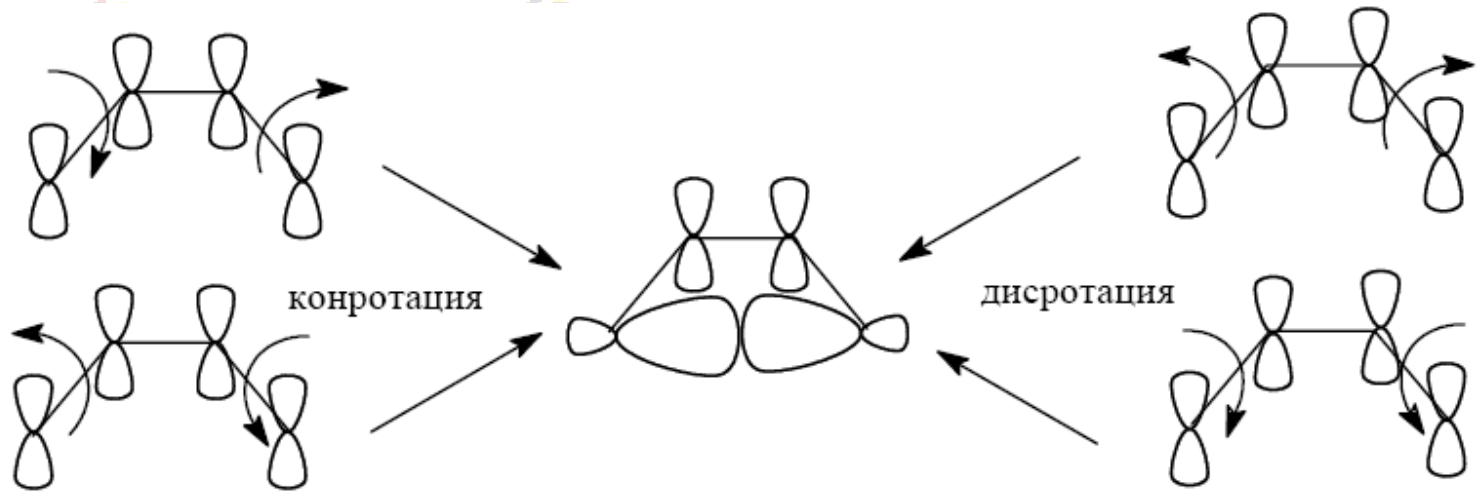
Фотохимически гетерированные *транс*-диенофилы



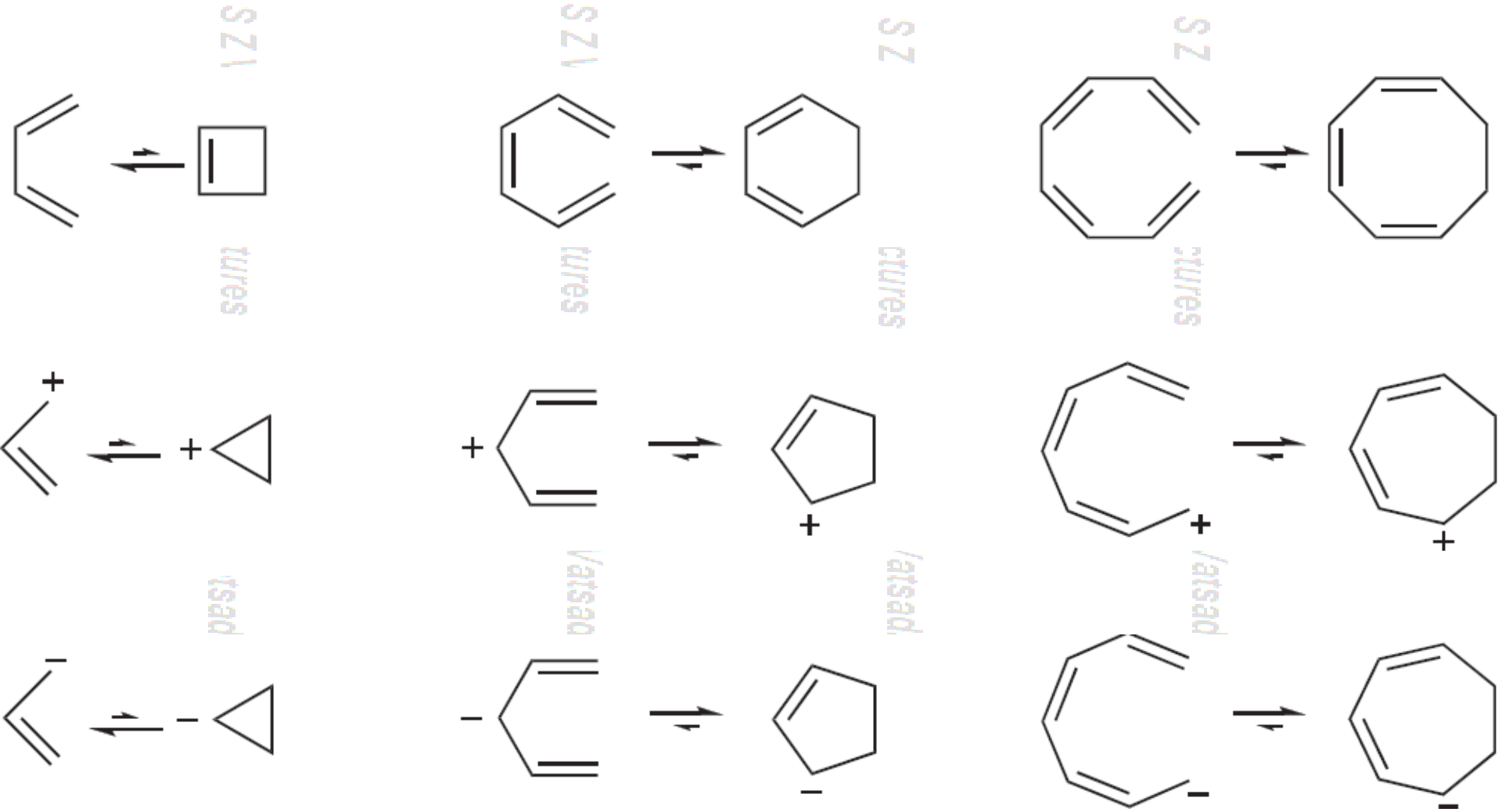
- Избранные примеры: 1,3-диполи



• Электроциклические реакции



• Электроциклические реакции

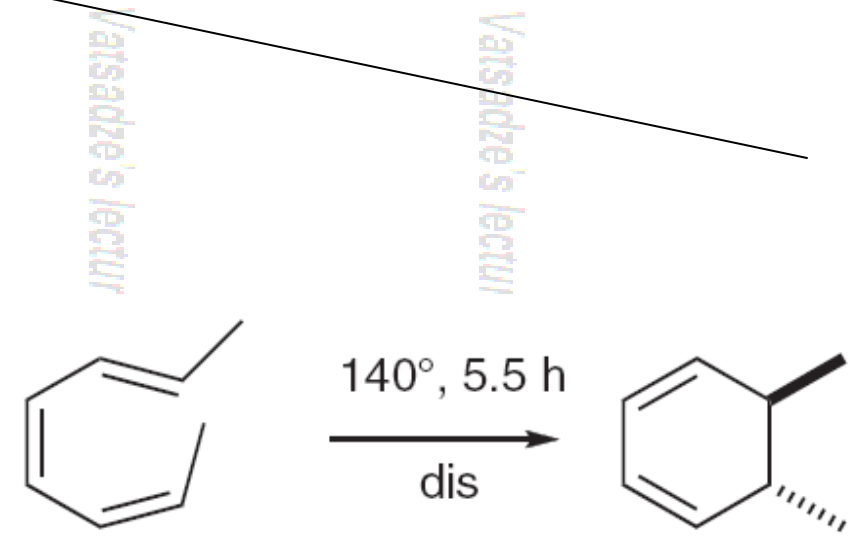
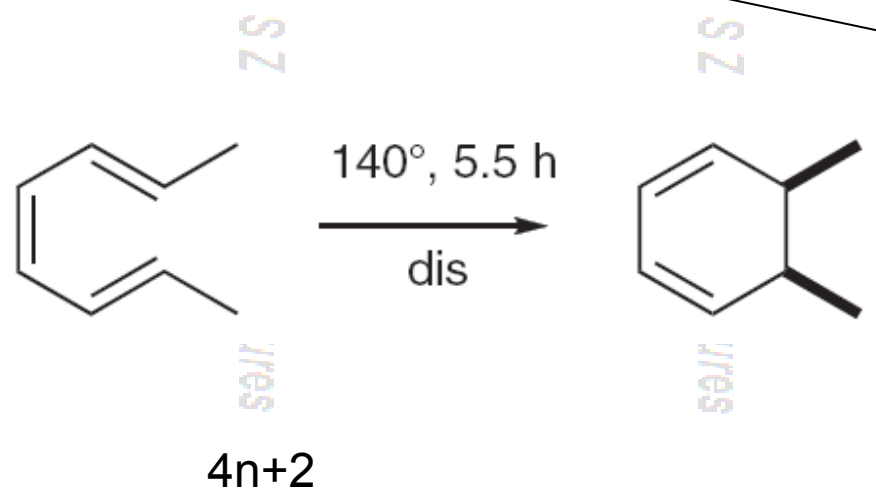
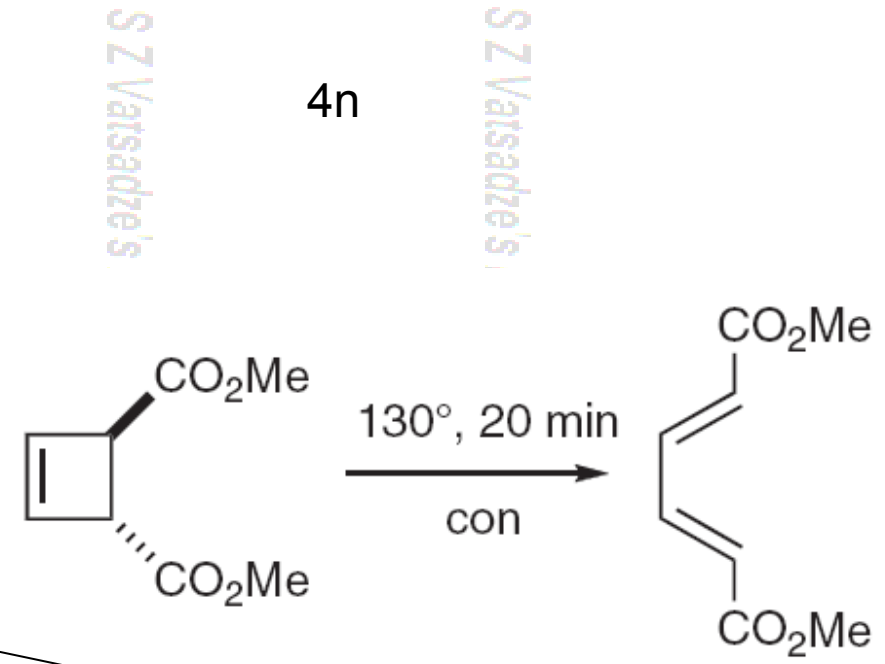
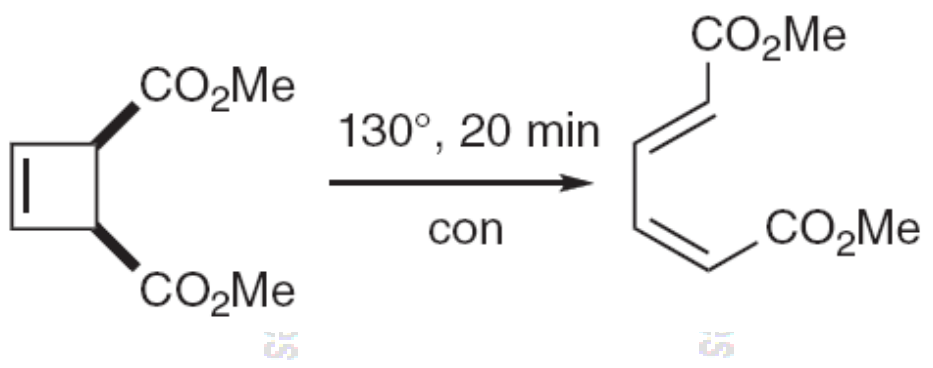


- Электроциклические реакции

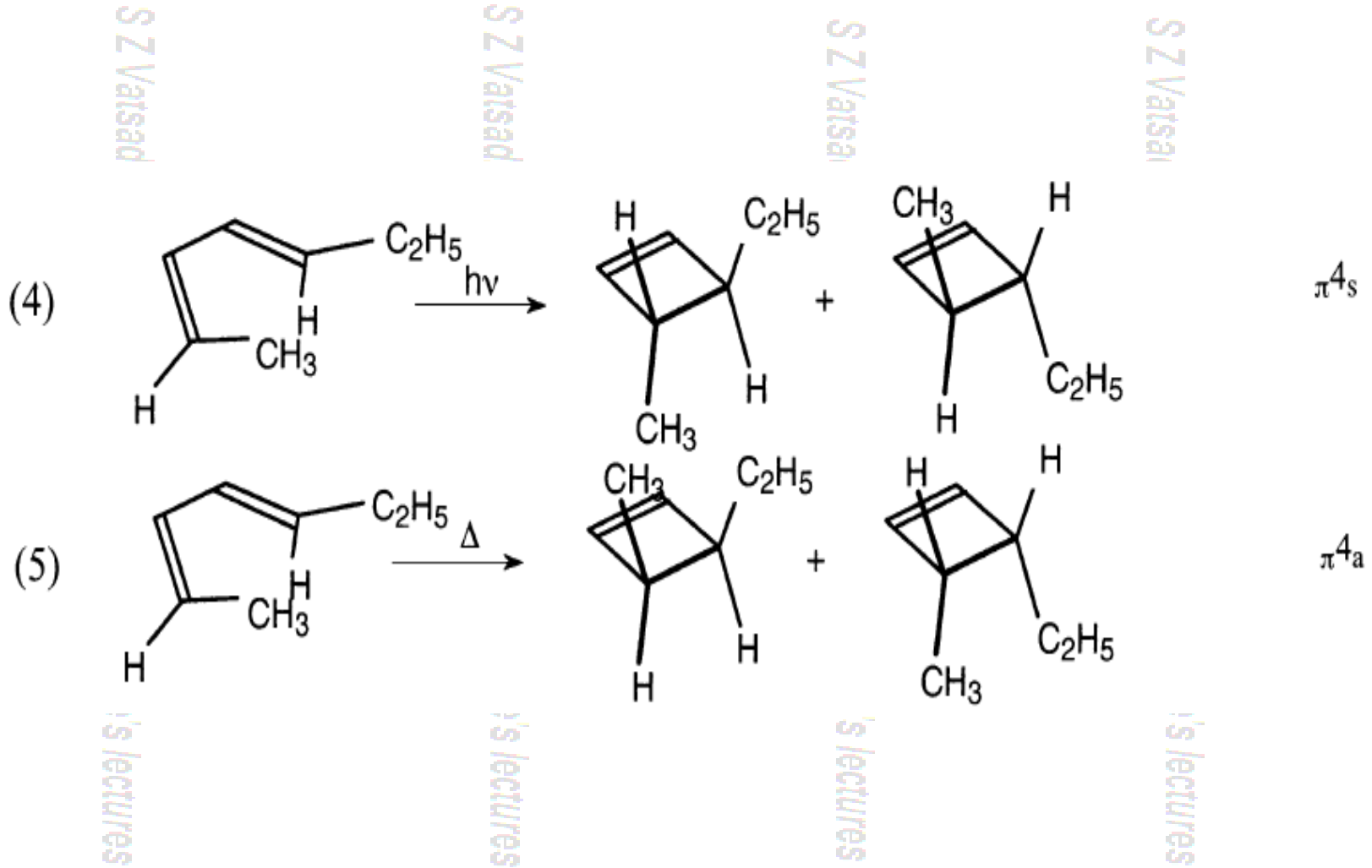
Parent equilibrium	Electrons	Stereochemistry
Butadiene = cyclobutene	4	conrotatory
Hexatriene = cyclohexadiene	6	disrotatory
Octatetraene = cyclooctatriene	8	conrotatory
Decapentaene = cyclodecatetraene	10	disrotatory
Cyclopropyl cation = allyl cation	2	disrotatory
Cyclopropyl anion = allyl anion	4	conrotatory
Pentadienyl cation = cyclopentenyl cation	4	conrotatory
Pentadienyl anion = cyclopentenyl anion	6	disrotatory
Heptatrienyl cation = cycloheptadienyl cation	6	disrotatory
Heptatrienyl anion = cycloheptadienyl anion	8	conrotatory
Nonatetraenyl cation = cyclononatrienyl cation	8	conrotatory
Nonatetraenyl anion = cyclononatrienyl anion	10	disrotatory

Если количество электронов в термической реакции $4n+2$, то она разрешена дисротаторно, если $4n$ – то конротаторно.

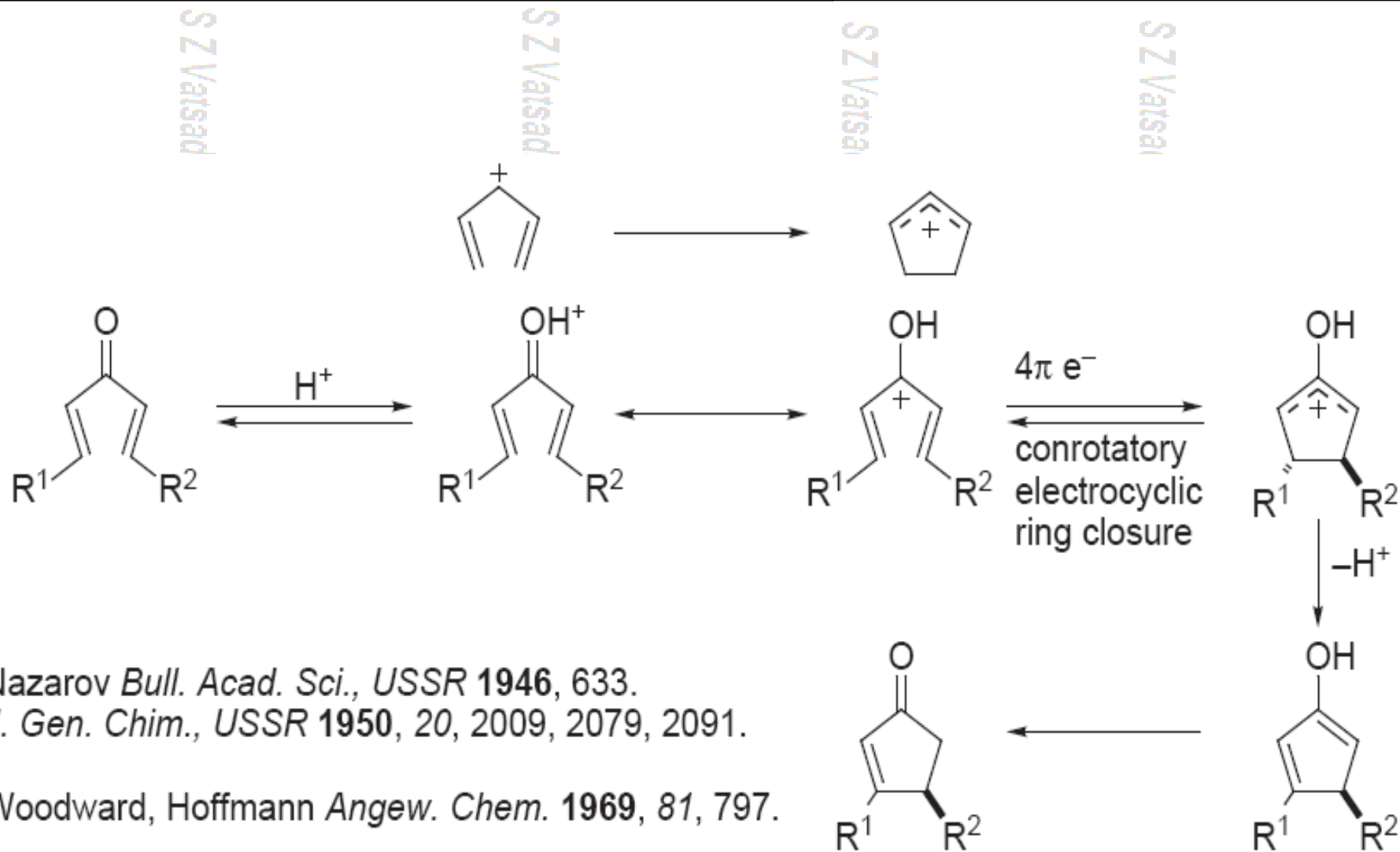
• Электроциклические реакции



Сравнение стереохимии термических и фотохимических



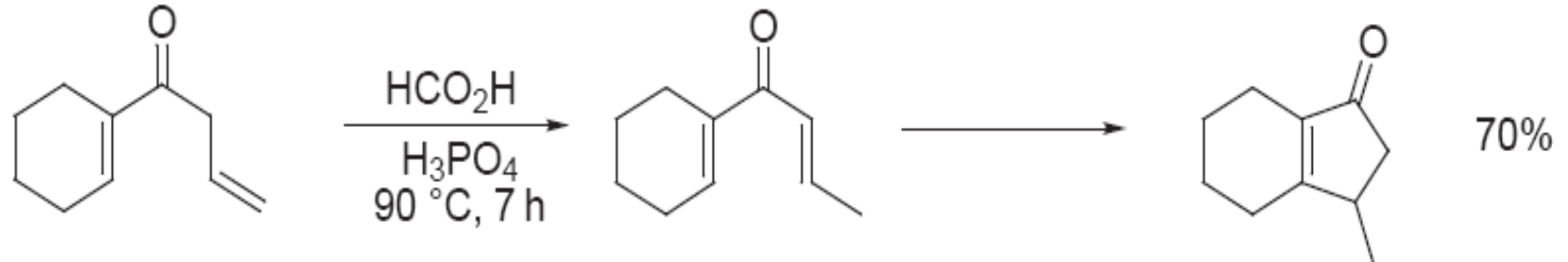
• Циклизация по Назарову



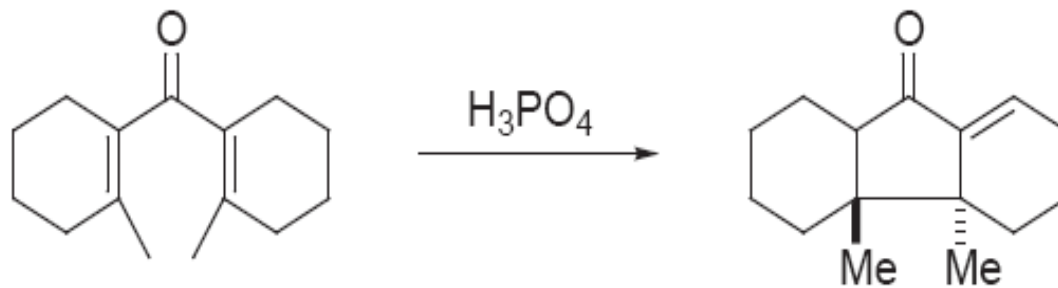
Nazarov *Bull. Acad. Sci., USSR* **1946**, 633.
J. Gen. Chim., USSR **1950**, 20, 2009, 2079, 2091.

Woodward, Hoffmann *Angew. Chem.* **1969**, 81, 797.

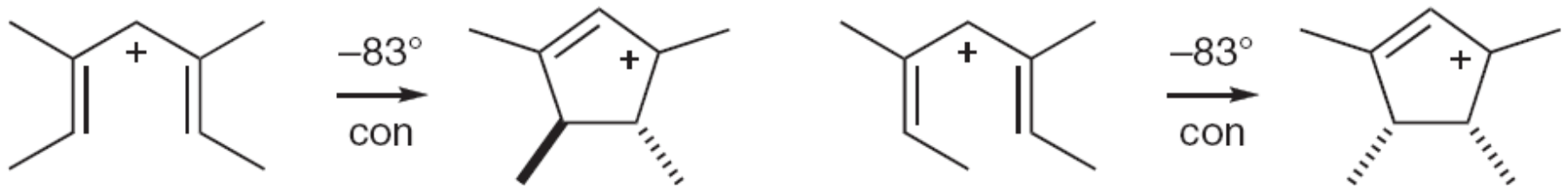
• Циклизация по Назарову



Nazarov *Chem. Abstr.* 1948, 42, 7731a, 7731h, 7732g, 7733e, 7734a, 7734.

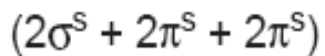


Braude *J. Chem. Soc.* 1953, 2202.

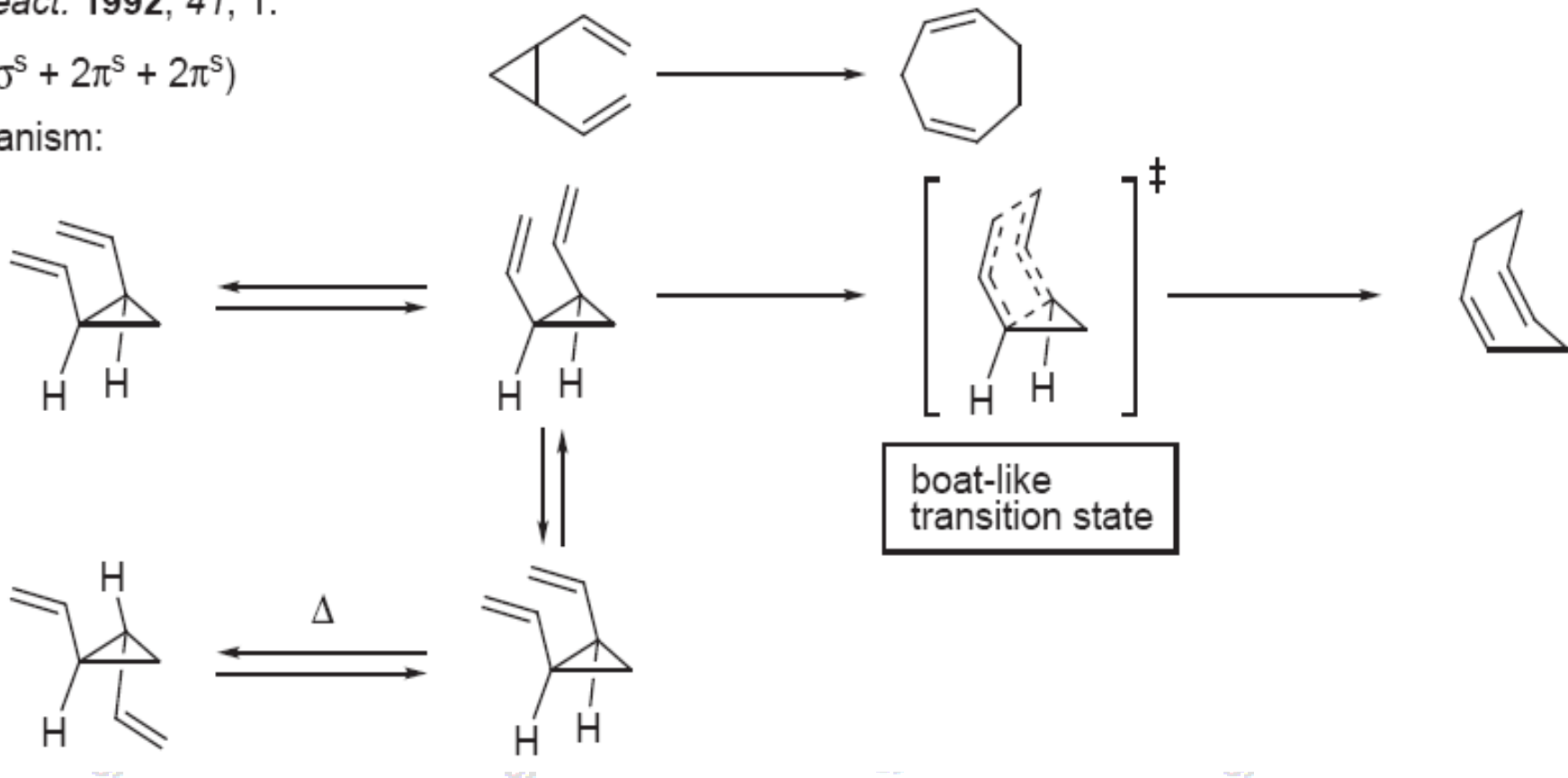


• Дивинилциклопропан

Comprehensive Org. Syn., Vol. 5, 971.
Org. React. 1992, 41, 1.



- Mechanism:



Электроциклическая или сигматропная?