Synthetic Year in Review: JACS 1977

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Most cited papers

ALLINGER NL
CONFORMATIONAL-ANALYSIS .130. MM2 - HYDROCARBON FORCE-FIELD UTILIZING V1 AND V2 TORSIONAL TERMS
Times Cited: 3300

DEWAR MJS, THIEL W
GROUND-STATES OF MOLECULES .39. MNDO RESULTS FOR MOLECULES CONTAINING HYDROGEN, CARBON, NITROGEN, AND OXYGEN
Times Cited: 2093

KALYANASUNDARAM K, THOMAS JK
ENVIRONMENTAL EFFECTS ON VIBRONIC BAND INTENSITIES IN PYRENE MONOMER FLUORESCENCE AND THEIR APPLICATION IN STUDIES OF MICELLAR SYSTEMS
Times Cited: 1506

KAMLET MJ, ABBOUD JL, TAFT RW
SOLVATOCHROMIC COMPARISON METHOD .6. PI-STAR SCALE OF SOLVENT POLARITIES
Times Cited: 759

OLMSTEAD WN, BRAUMAN JI
GAS-PHASE NUCLEOPHILIC DISPLACEMENT-REACTIONS
Times Cited: 646

VINEYARD BD, KNOWLES WS, SABACKY MJ, et al.
ASYMMETRIC HYDROGENATION - RHODIUM CHIRAL BISPHOSPHINE CATALYST
Times Cited: 530

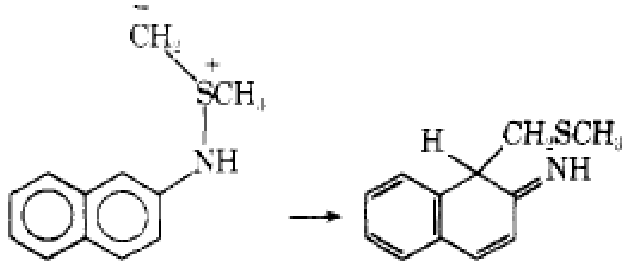
FRYZUK MD, BOSNICH B
ASYMMETRIC SYNTHESIS - PRODUCTION OF OPTICALLY-ACTIVE AMINO-ACIDS BY CATALYTIC-HYDROGENATION
Times Cited: 502

Most Prolific Authors:

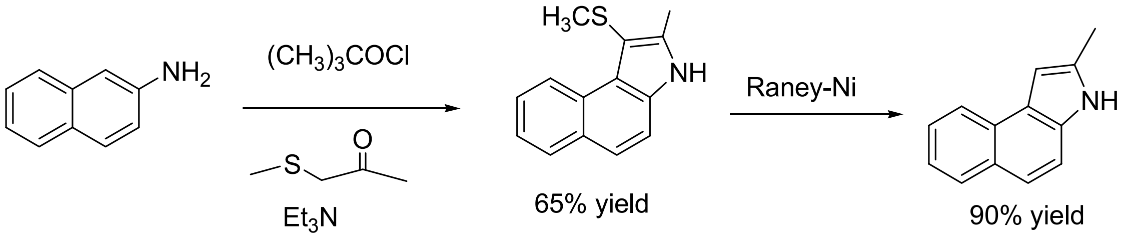
DEWAR, MJS (19)	HEHRE, WJ (11)
PAQUETTE, LA (18)	OLAH, GA (11)
BROWN, HC (14)	TAFT, RW (11)
COTTON, FA (13)	IBERS, JA (10)
BRUICE, TC (11)	TROST, BM (10)
CLARDY, J (11)	BERGMAN, RG (8)

Methodology

Gassmann – 2, 3 sigmatropic rearrangement

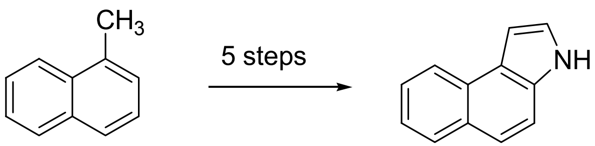


efficient way to make polycyclic aromatic indoles



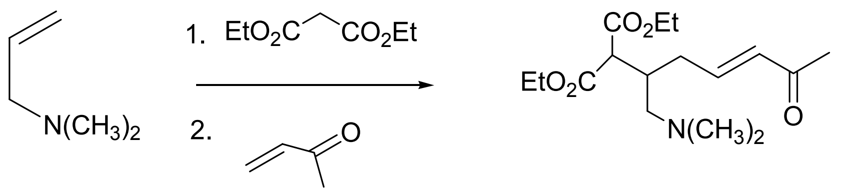
59% overall yield

Compare to:



10% overall yield

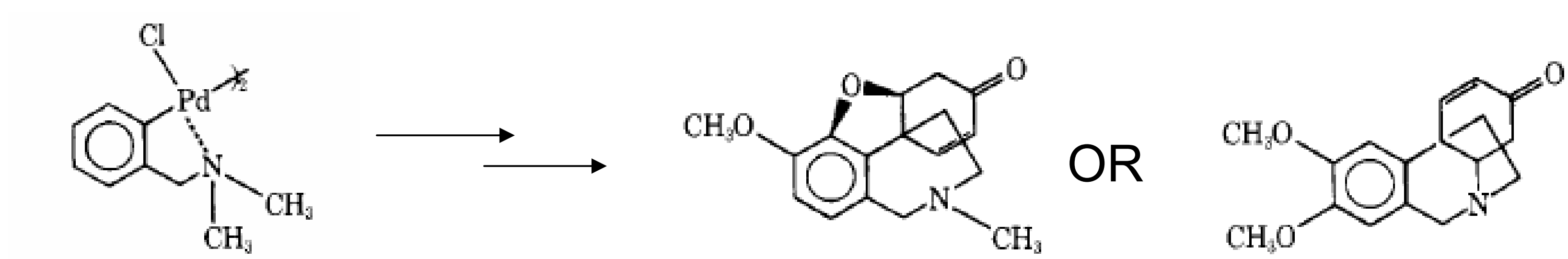
Holton – Regiospecific Palladation (2 papers – pp.4175-4179)



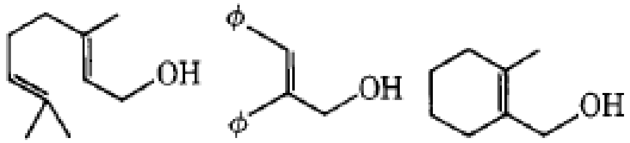
82% yield

selective beta addition of carbon nucleophiles to
allylic amines and allylic sulfides

Selective ortho aromatic coupling

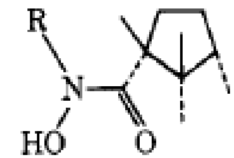


Sharpless epoxidation



2 3 4

VO(acac)$_2$ (1 mol%), *t*BuOOH → epoxide



1a, R = CH_3
1b, R = Ph
1c, R = 2,6-Me_2Ph

Hydroxamic acid (equiv)[b]	Allylic alcohol	°C	% ee[c]	% conversion[d]
1 **1a** (5)	**2**	−78 → 25	17	83
2 **1a** (3)	**3**	−78 → 25	10	100
3 **1a** (5)	**3**	−78 → 25	21	80
4 **1a** (10)	**3**	−78 → 25	18	22
5 **1b** (4)	**2**	−78 → 25	19	100
6 **1b** (4)	**2**	25	17.5	100
7 **1b** (5)	**2**	25	30	86
8 **1b** (5)	**2**	−78	—	0
9 **1b** (7)	**2**	−78 → 25	10	10
10 **1b** (1)	**3**	−78 → 25	<8	100
11 **1b** (2)	**3**	−78 → 25	8	100
12 **1b** (3)	**3**	−78 → 25	22.5	100
13 **1b** (5)	**3**	−78 → 25	50	30
14 **1b** (5)	**3**	25	40	84
15 **1b** (5)	**4**	25	40	87
16 **1b** (5)	**4**	−10	44	75
17 **1c** (3)	**2**	0	5	70
18 **1c** (4)	**2**	0	19	55
19 **1c** (5)	**2**	0	—	0

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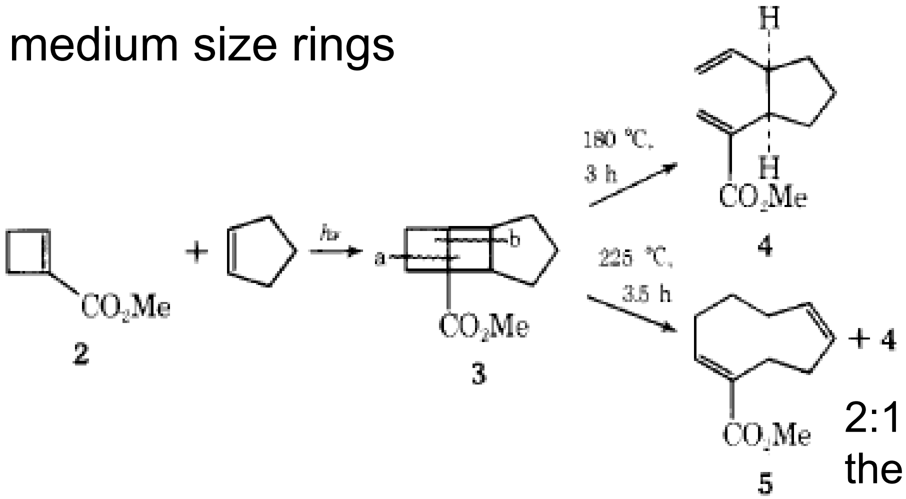
Wender – Preparation of 1,5 dienes

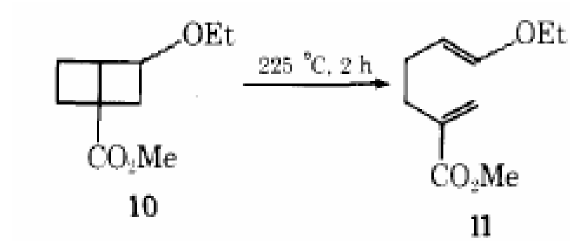
Key Point: interesting thermal cleavage followed by Cope rearrangement

medium size rings

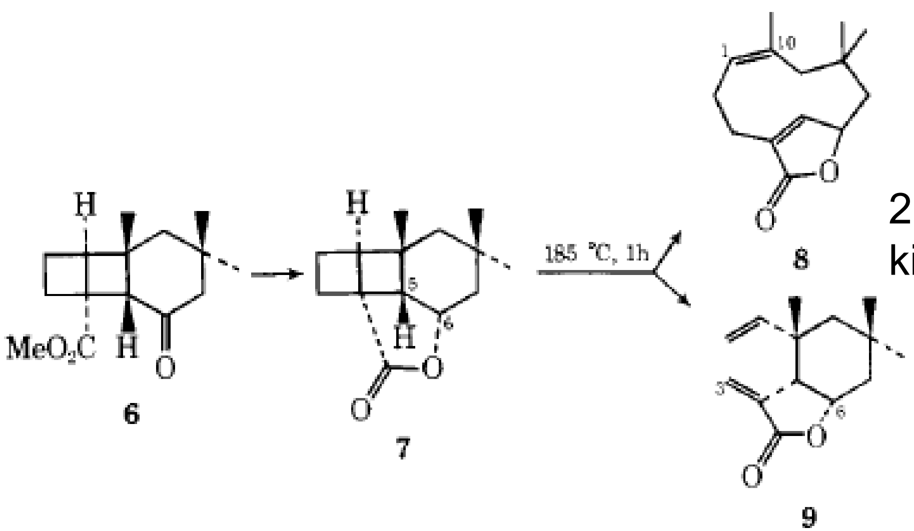


2:1 mixture of 4/5
thermodyamic control

acylic dienes



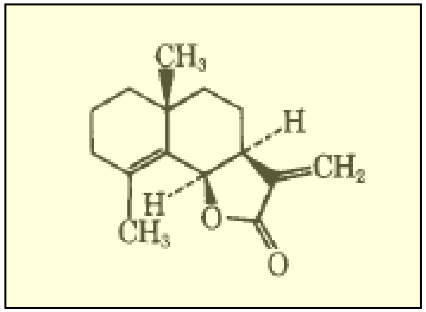
only product



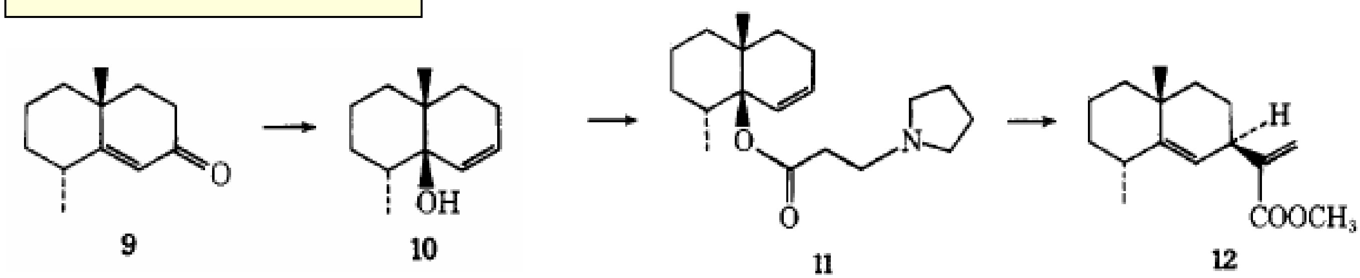
2:1 mixture of 8/9
kinetic control

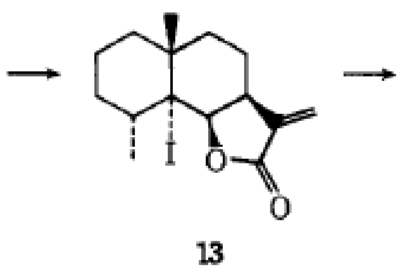
when heated to 240 °C for 12hrs
a 1:2 ratio of 8/9 is obtained

Still - Frullanolide



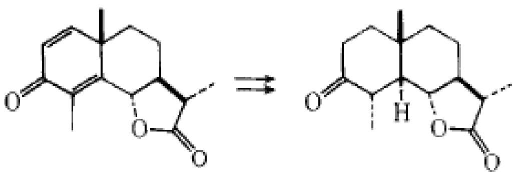
Key point:
Claisen rearrangement to install tertiary stereocenter





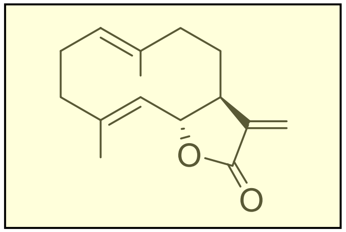
Frullanolide

Grieco – Costunolide (p. 1717)

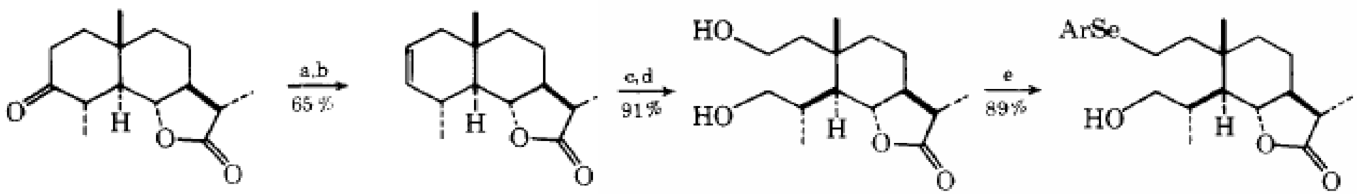


santonin 5 → 6

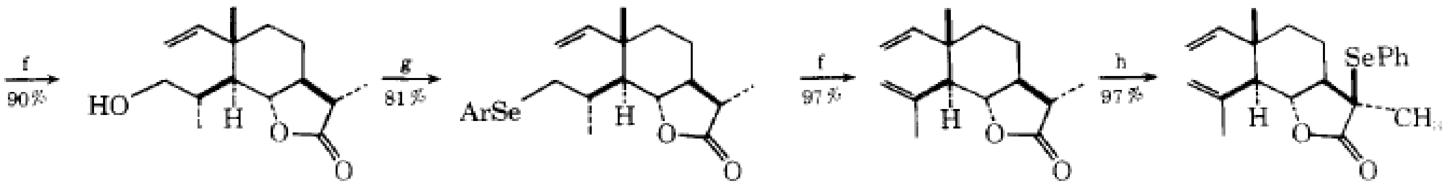
2 steps
-hydrogenation
-epimerization



(+)-costunolide

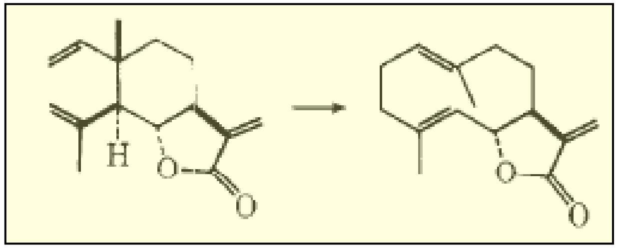


6 7 8 9



10 11 3 12

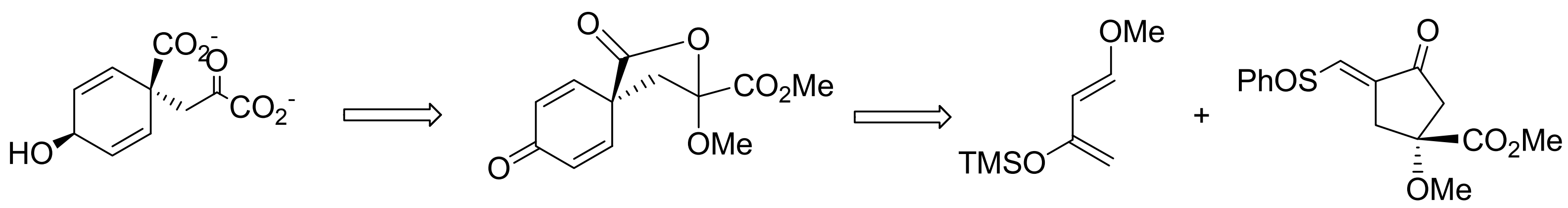
12 →



1 2

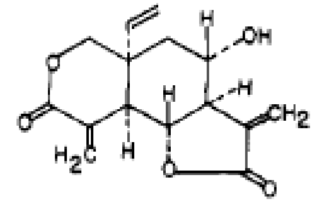
Key Points:
-asymmetric synthesis starting from santonin
-Cope rearrangement

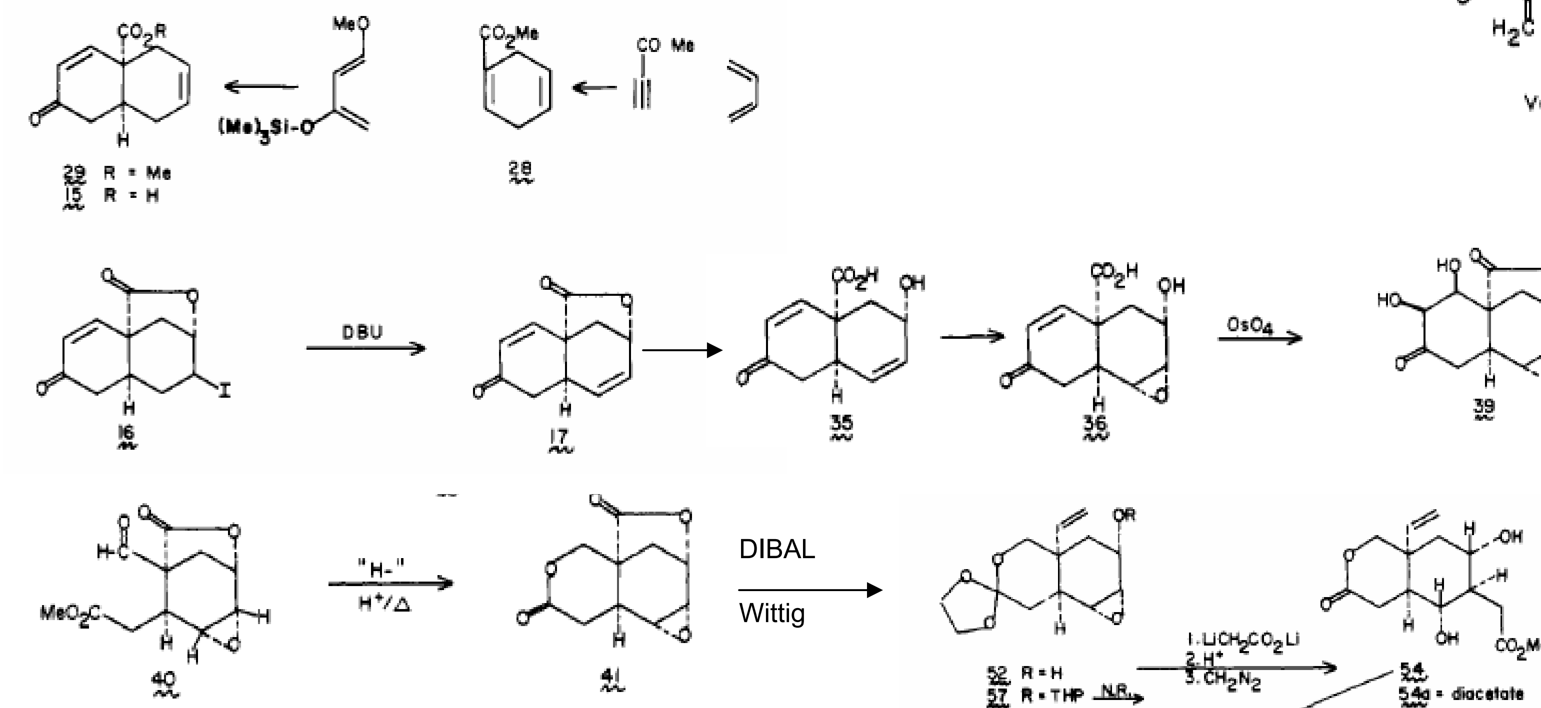
Danishefsky - Prephenate

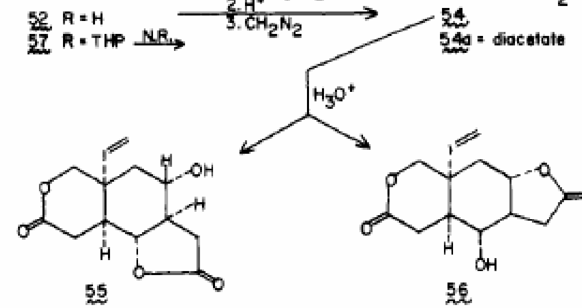


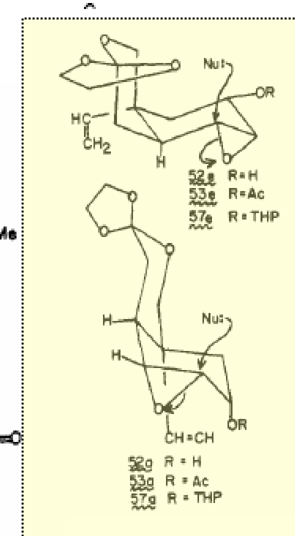
key point:
use of Danishefsky
diene to access quaternary center

Danishefsky – Vernolepin (p. 6066)





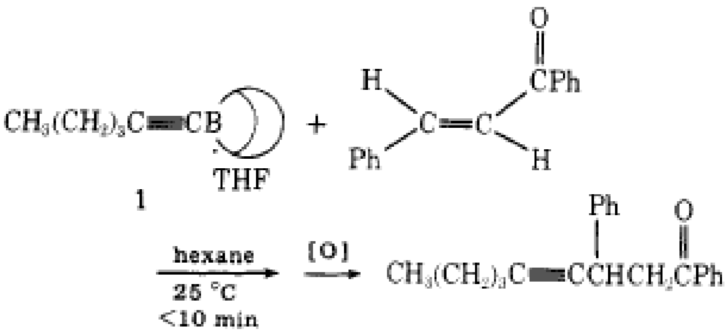


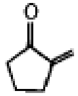
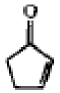
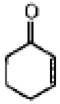


key points:

1. use of Diels-Alder to access decalin system
2. directed epoxidation
3. conformationally directed epoxide opening
4. α-methylenation with Eschenmoser's salt

Brown, Molander, Sinclair – conjugate addition of boranes (p. 954)

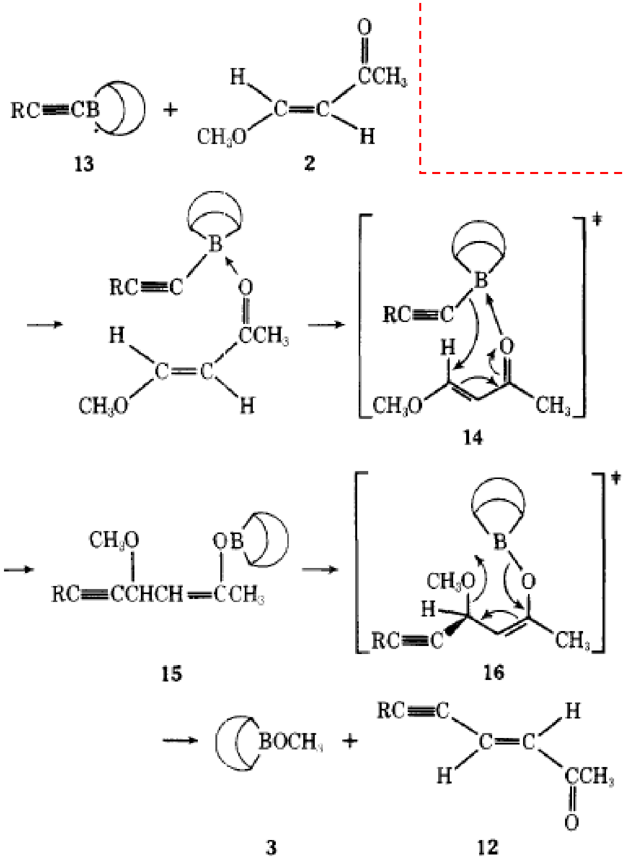


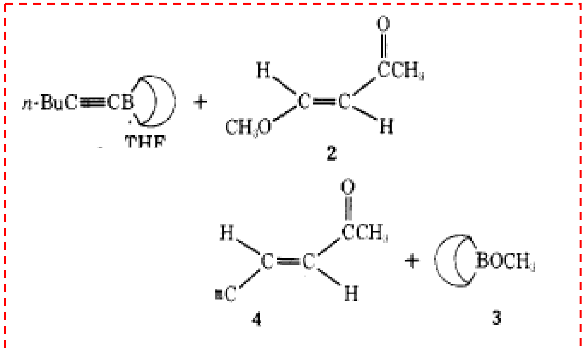
$CH_2{=}CHCOCH_3$ (4)	10 min	96
$CH_3CH{=}CHCOCH_3$ (5)	1 h	100
$(CH_3)_2CH{=}CHCOCH_3$ (6)	5 days	70
 (7)	10 min	70
 (8)	3 days	0^d
 (9)	3 days	0^d

mechanism:

ref: JOC, 1977, 42 (18), 3106

Scheme I





Key point: stereospecific conjugate addition of boranes

Note: Brown retired in 1978 and won the Nobel Prize in 1979

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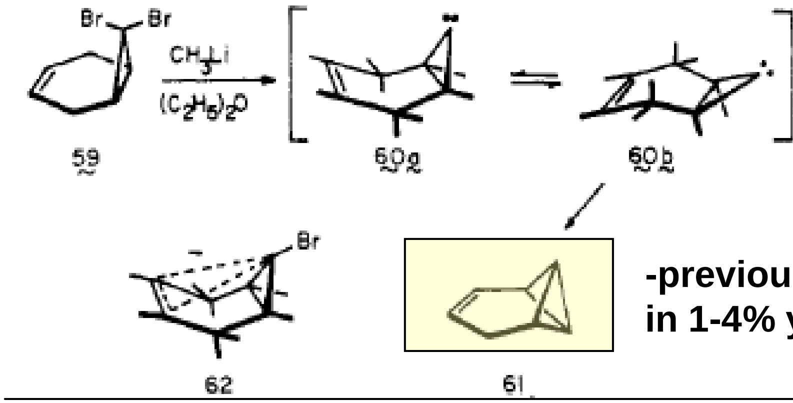
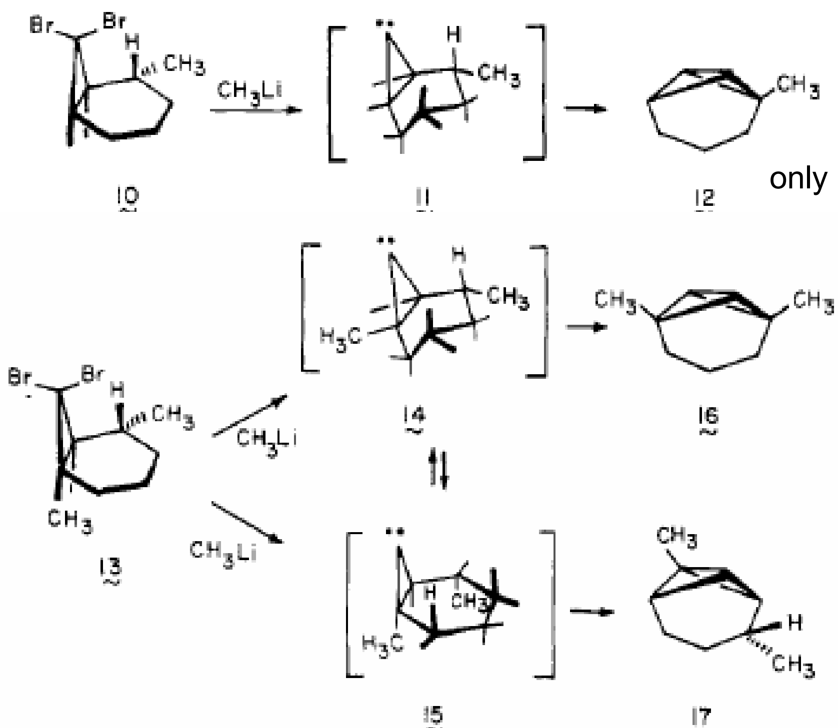
Paquette – Strained hydrocarbons (p. 5709)



-previously obtained in 1-4% yields

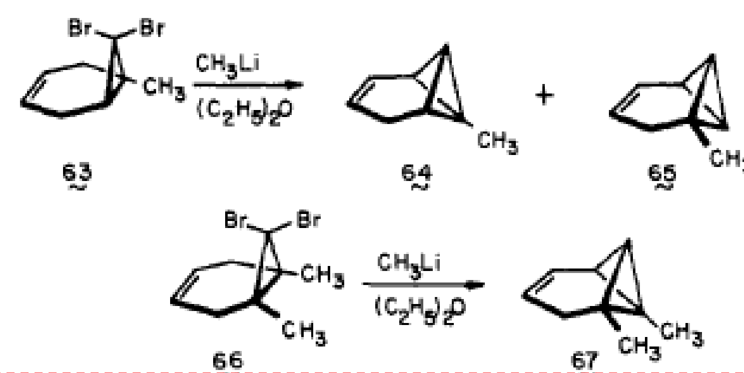
key points:

1. methyl group at bridging carbon allows access to tricyclo[4.1.0.0]hept-3-ene systems
2. observation of hyperconjugation effects???

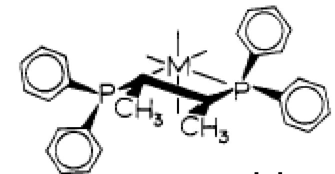


only product

9:1 ratio of 16/17

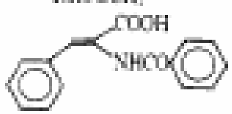
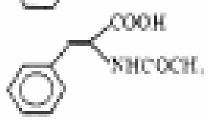
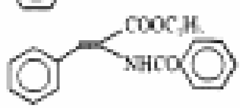
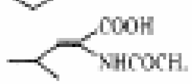
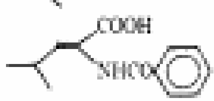
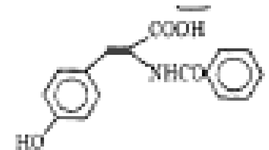
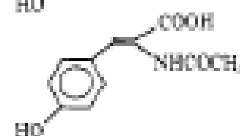
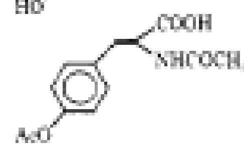
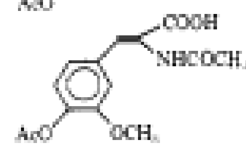


Bosnich - Asymmetric Hydrogenation (p. 6262)



chiraphos

Table I. Optical Yields (%)[a]

Amino acid	Substrate	Solvent THF	Solvent EtOH	Solvent Other
Alanine		88	91	
Phenylalanine		99	95	
		74	89	
		83		
Leucine		100	93	
		87	72	88 (benzene)
Tyrosine		92		84 (dioxane)
		80	88	91 (1:1, EtOH/ H_2O) 78 (MeOH)
		74	88	
DOPA		80	83	

quantitative conversion for all substrates

key points:

1. bidentate ligand to induce chirality in hydrogenation
2. very high "optical yields" of amino acids