

JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 95, NUMBER 1

JANUARY 10, 1973

Year in Review: JACS 1973

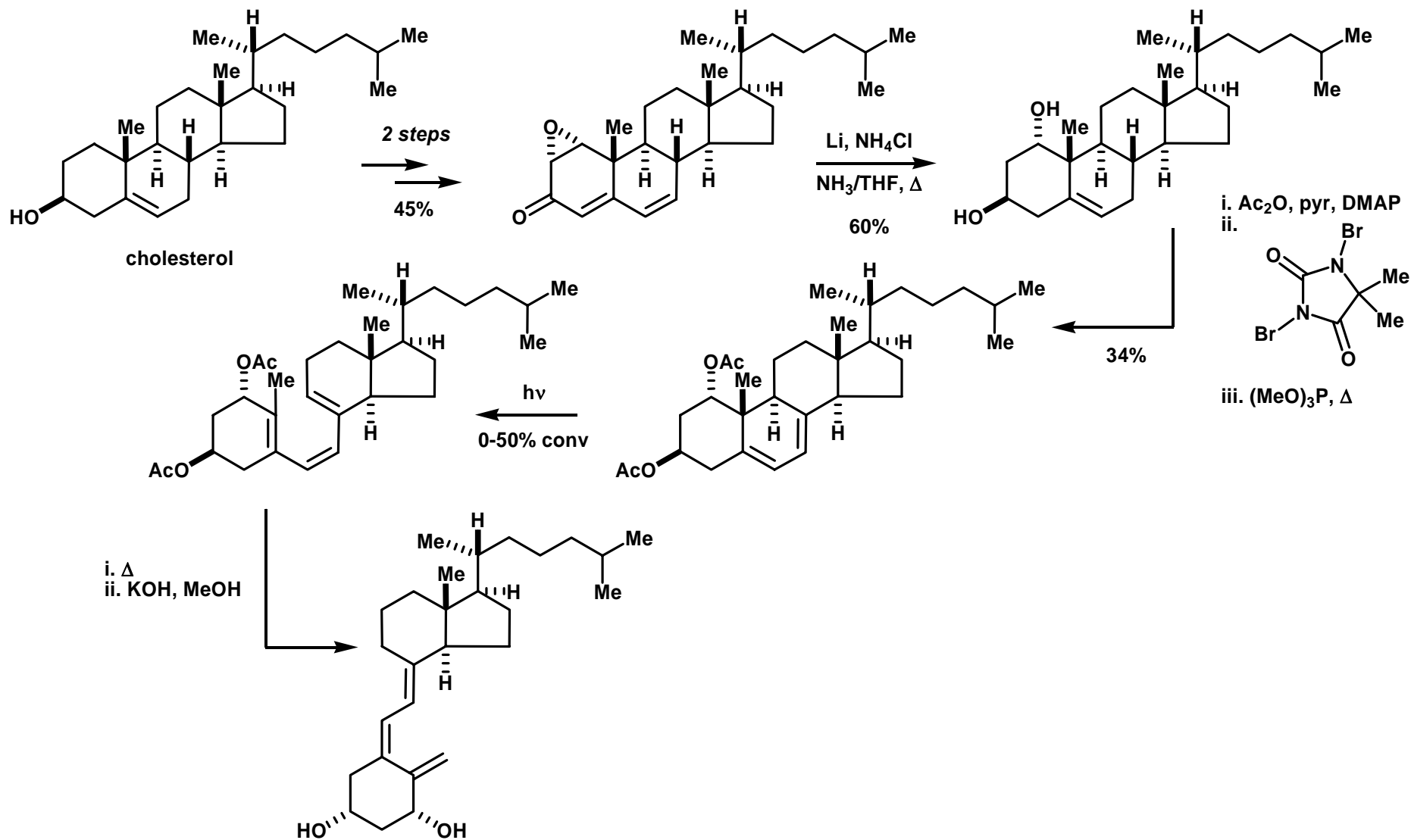
Peter K. Park
Laboratory of James L. Leighton

Year in Review Meeting #4
Friday, 30 June 2006

Some Statistics from the Science Citation Index

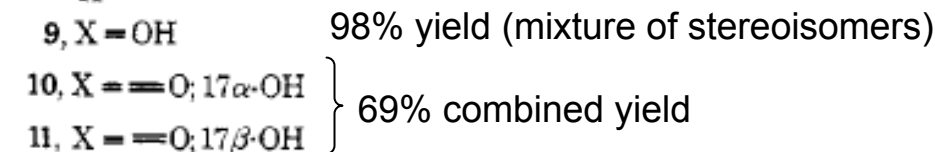
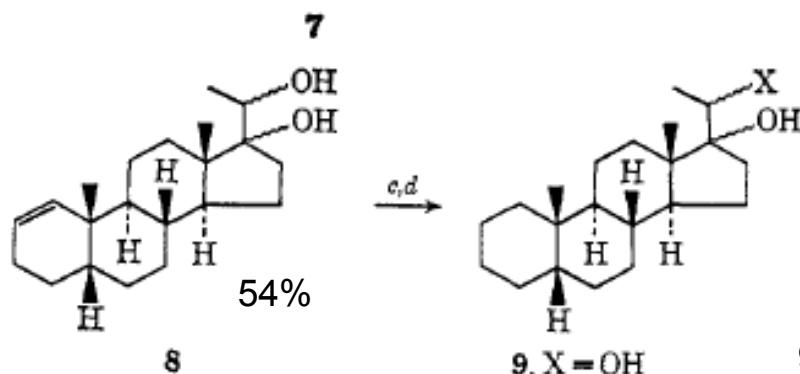
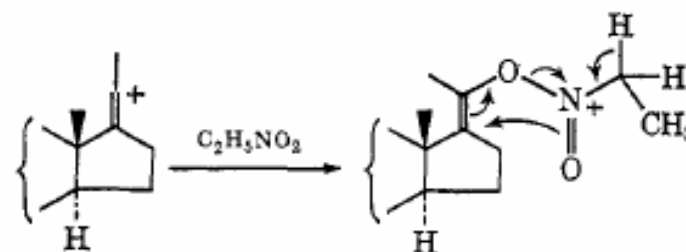
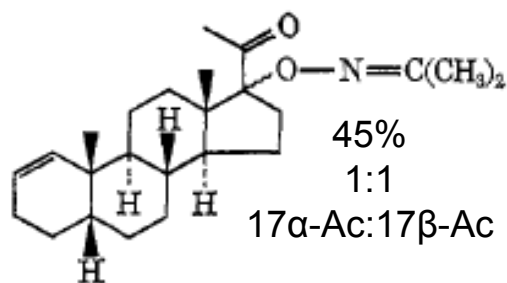
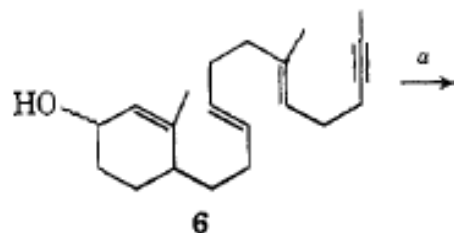
- Number of papers published in *J. Am. Chem. Soc.* in 1973: **2094**
- Most cited paper: **2074** citations!
Dale J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512
“Nuclear Magnetic Resonance Enantiomer Reagents. Configurational Correlations *via* Nuclear Magnetic Resonance Chemical Shifts Of Diastereomeric Mandelate, O-Methylmandelate, and α -Methoxy- α -trifluoromethylphenylacetate (MTPA) Esters”
- Top 25 most prolific authors of 1973:
 1. Olah, G. A. (24)
 2. Brown, H. C. (17)
 3. Trost, B. M. (16)
 4. Gassman, P. G. (14)
Ibers, J. A. (14)
 5. Cotton, F. A. (13)
Cram, D. J. (13)
Paquette, L. A. (13)
 6. Ingold, K. U. (11)
Kochi, J. K. (11)
Nelsen, S. F. (11)
 7. Mislow, K. (10)
Skell, P. S. (10)
 8. Baldwin, J. E. (9)
Collman, J. P. (9)
Dewar, M. J. S. (9)
Schleyer, P. V. (9)
Zimmerman, H. E. (9)
 9. Breslow, R. (8)
Clardy, J. (8)
Corey, E. J. (8)
Epiotis, N. D. (8)
Hawthorne, M. F. (8)
Johnson, C. R. (8)
Taylor, E. C. (8)

A Convenient Synthesis of 1 α -Hydroxy-Vitamin D₃



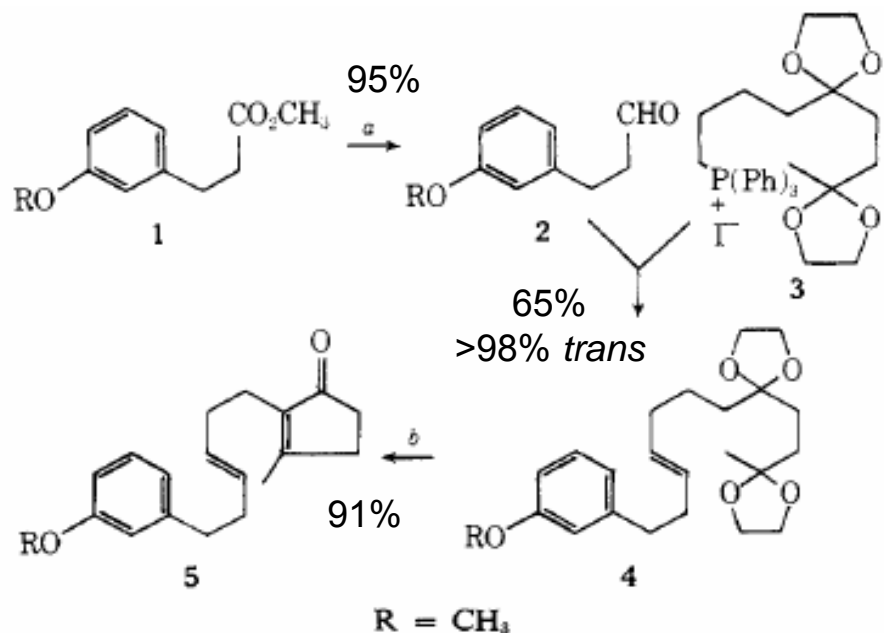
Acetylenic Bond Participation in Biogenetic-Like Olefinic Cyclizations in Nitroalkane Solvents.

Synthesis of the 17-Hydroxy-5 β -pregnan-20-one System

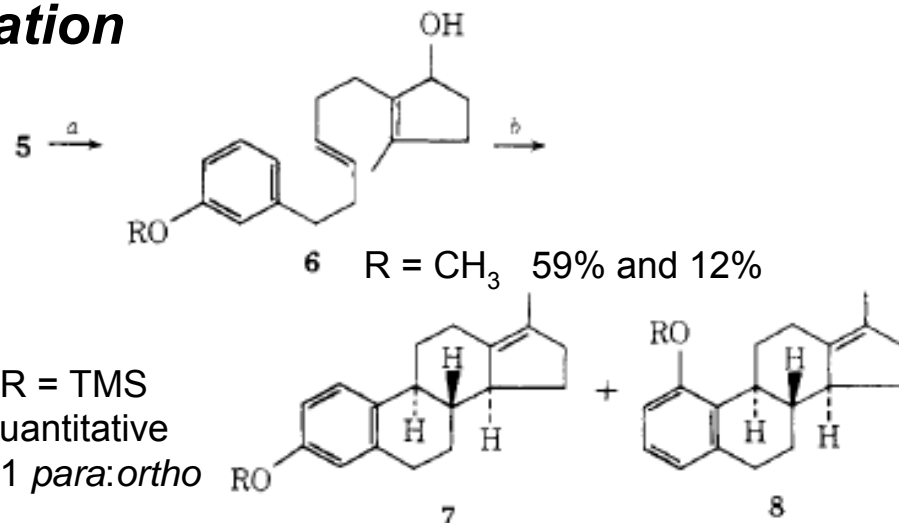


^a $\text{Cl}_2\text{CCO}_2\text{H}$, $(\text{CH}_3)_2\text{CHNO}_2$, N_2 , 0° , 4 hr. ^b LiAlH_4 , THF, N_2 , reflux, 2 hr. ^c To give 9: H_2 , 10% Pd/C, EtOAc, 23° . ^d To give 10 and 11: NBS, dioxane, H_2O , 23° , 5 hr.

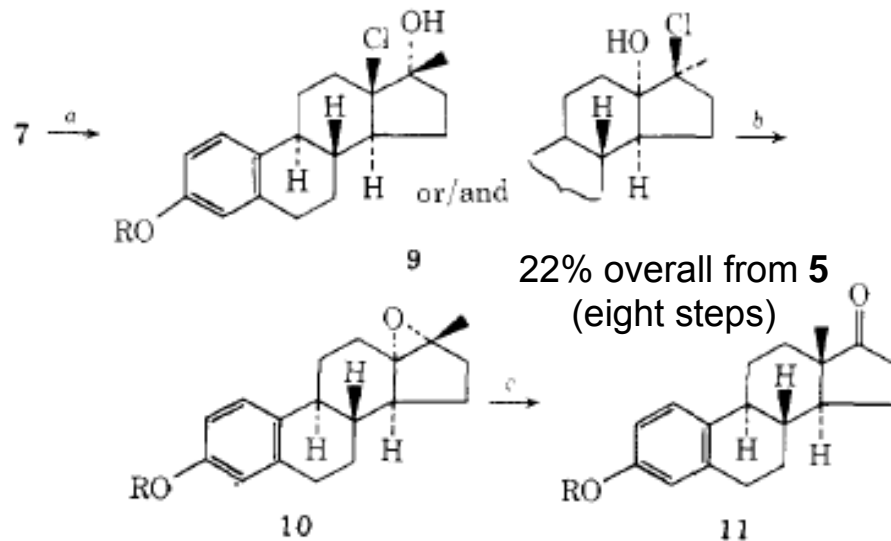
A Stereospecific Total Synthesis of Estrone via a Cationic Olefinic Cyclization



^a $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, THF, 3 hr, -75° . ^b 1:2 0.1 N HCl-EtOH, 5 hr, 50° , then 2 parts 0.1 M NaOH, 7 hr, reflux.

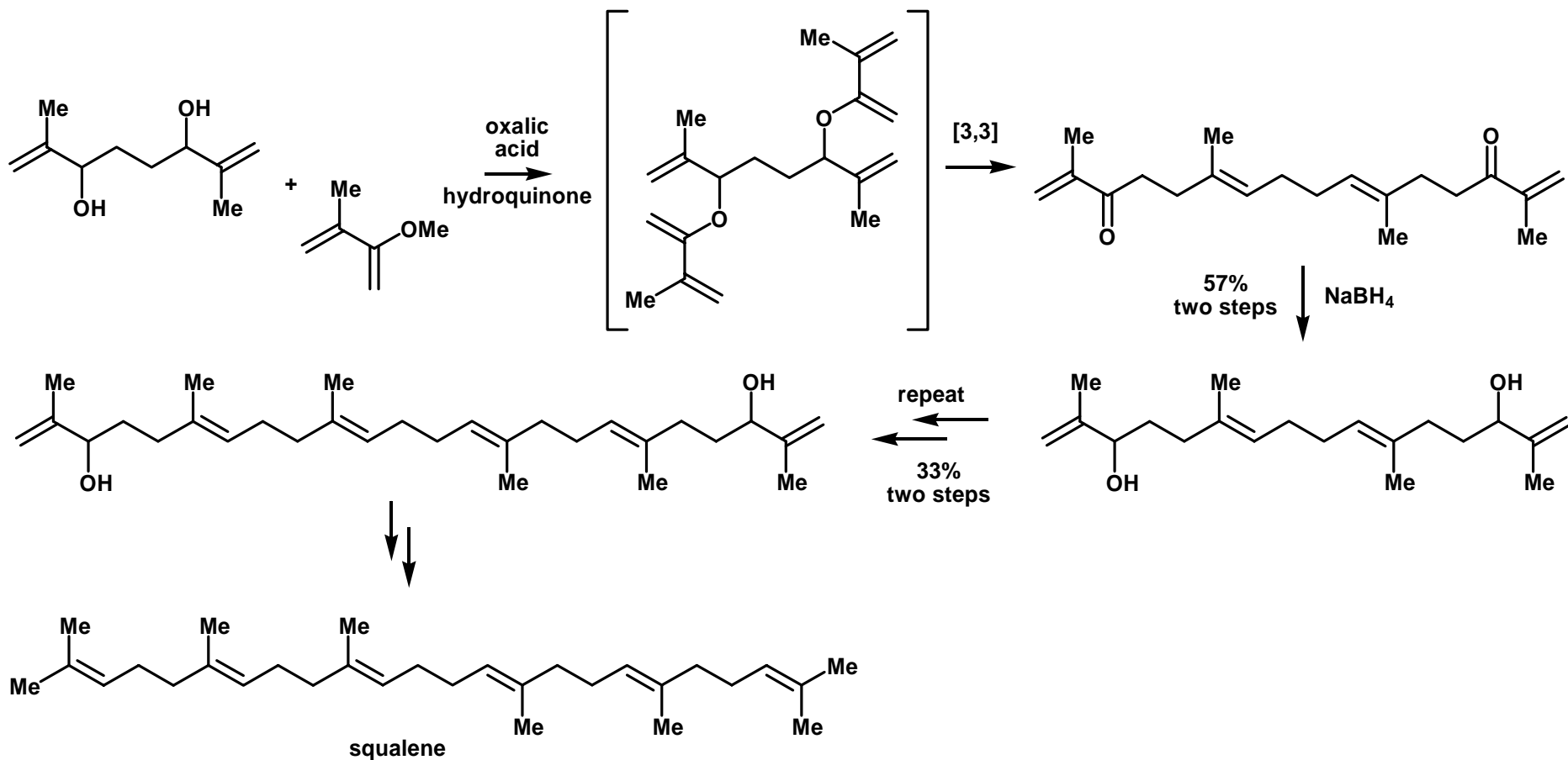


^a For R = CH_3 or H, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, THF, 30 min, 0° . ^b For R = TMS, 3 equiv of SnCl_4 , CH_2Cl_2 , 30 min, -100° .

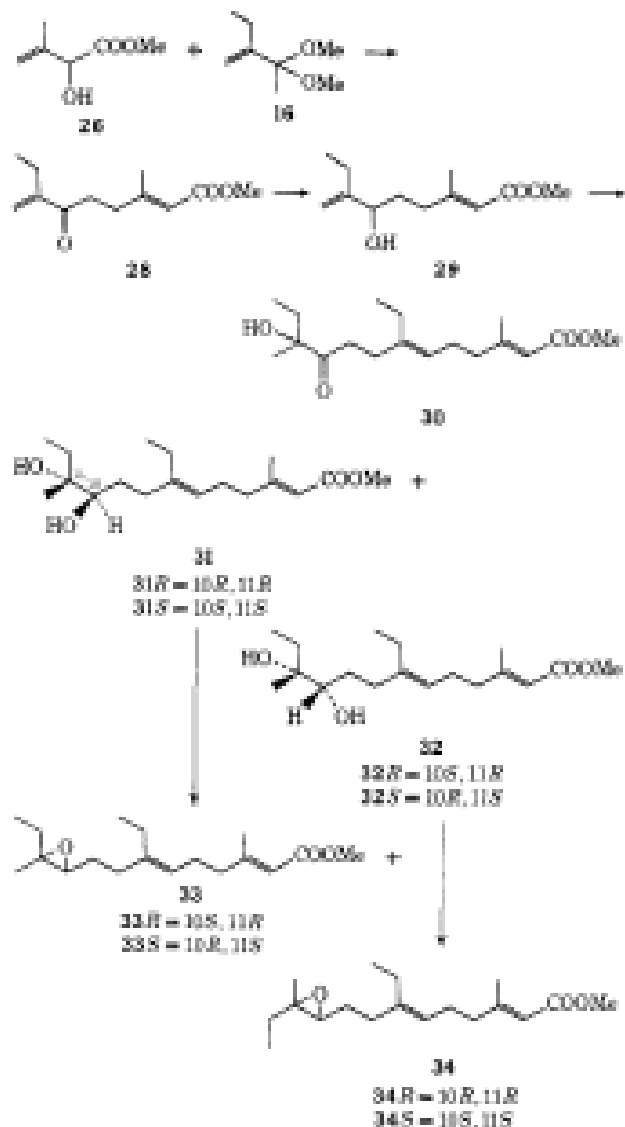


^a $p\text{-TsNCl}_2$, 1:9 $\text{H}_2\text{O}-\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, 10 min, 0° . ^b $(\text{CH}_3)_4\text{NOH}$, aqueous acetone, 2 hr, 25° . ^c $\text{BF}_3 \cdot \text{Et}_2\text{O}$, benzene, 1 min, 25° .

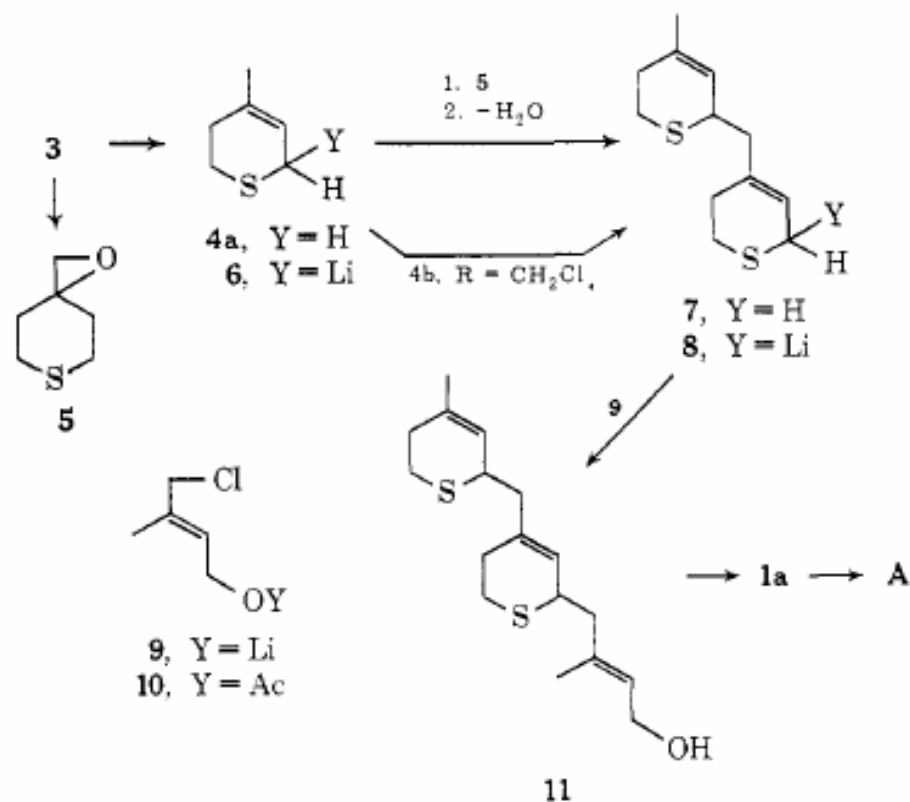
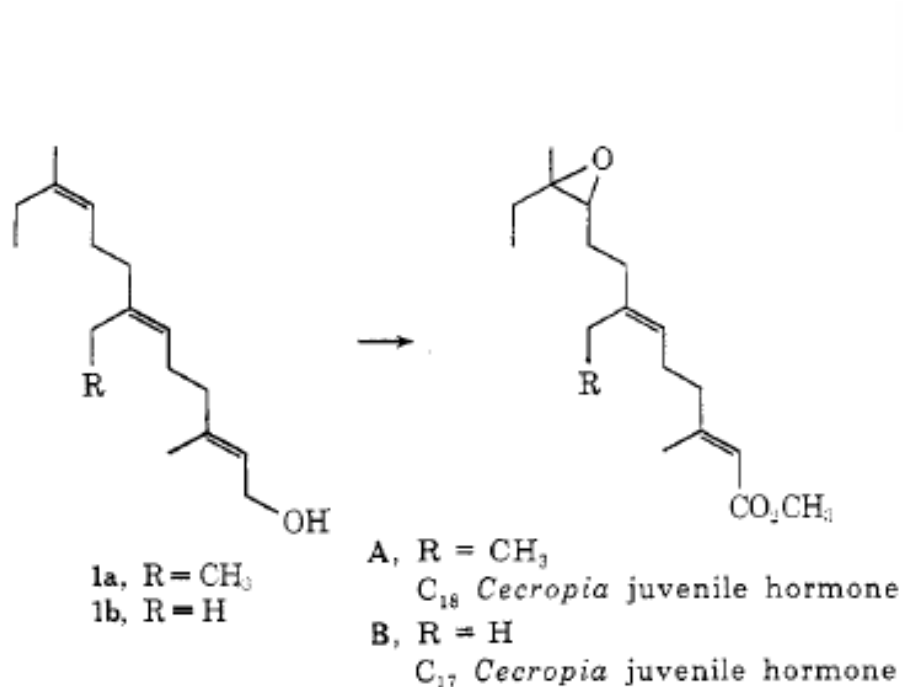
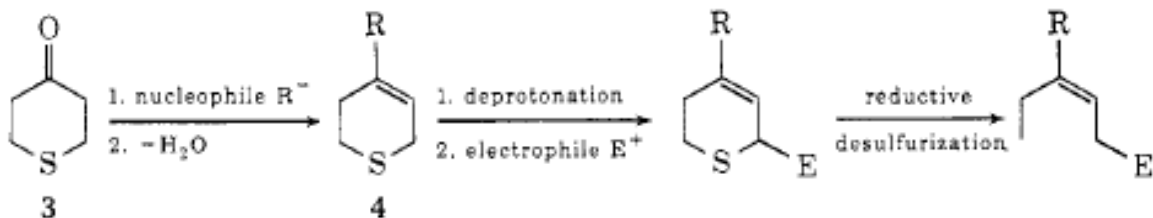
Application of the Claisen Rearrangement to the Synthesis of Trans Trisubstituted Olefinic Bonds. Synthesis of Squalene and Insect Juvenile Hormone



Application of the Claisen Rearrangement to the Synthesis of Trans Trisubstituted Olefinic Bonds. Synthesis of Squalene and Insect Juvenile Hormone

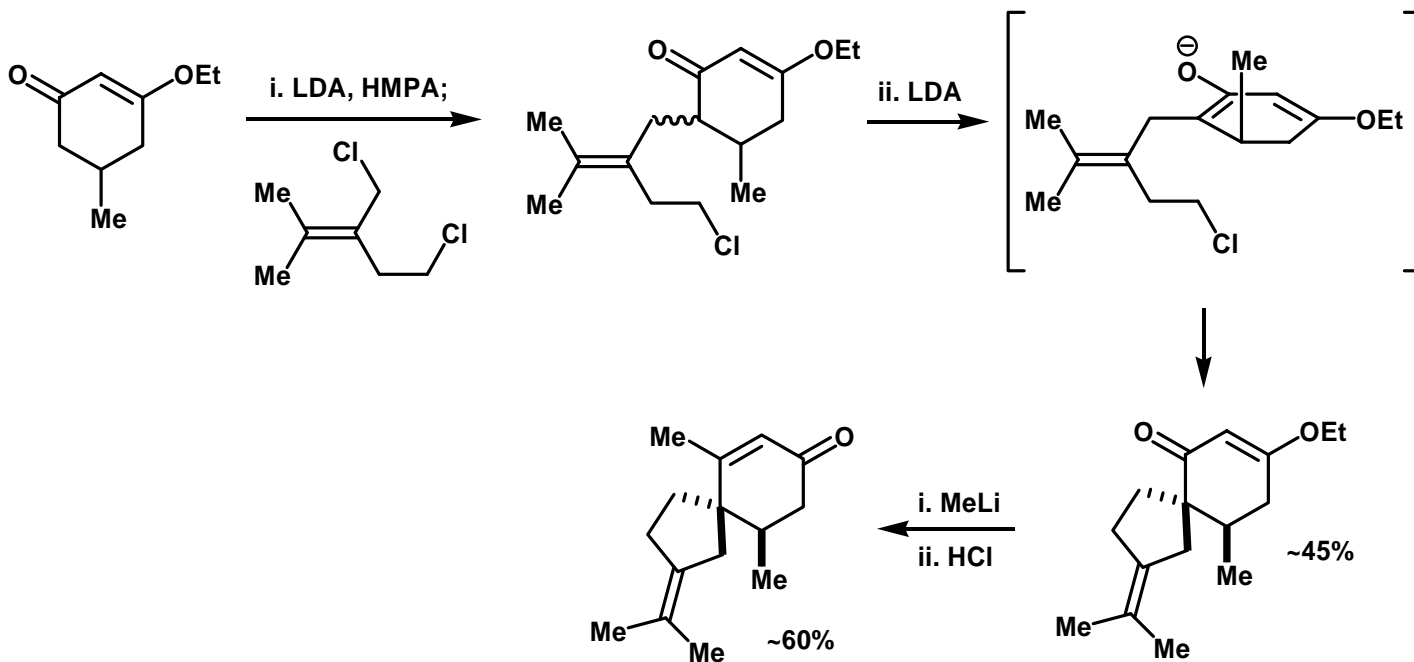
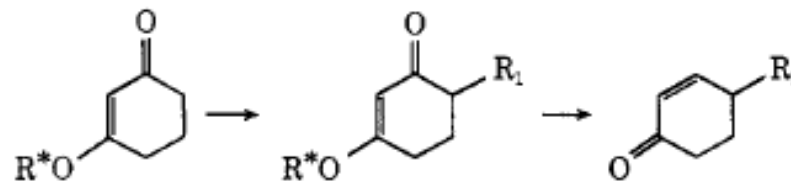


New Thiane Chemistry. The Conceptually Simple and Technically Practical Total Synthesis of Cecropia Juvenile Hormones

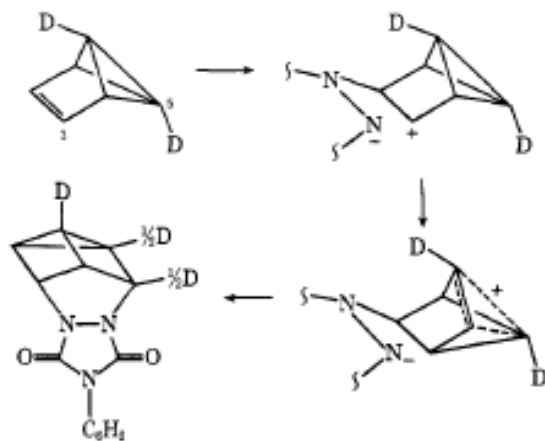
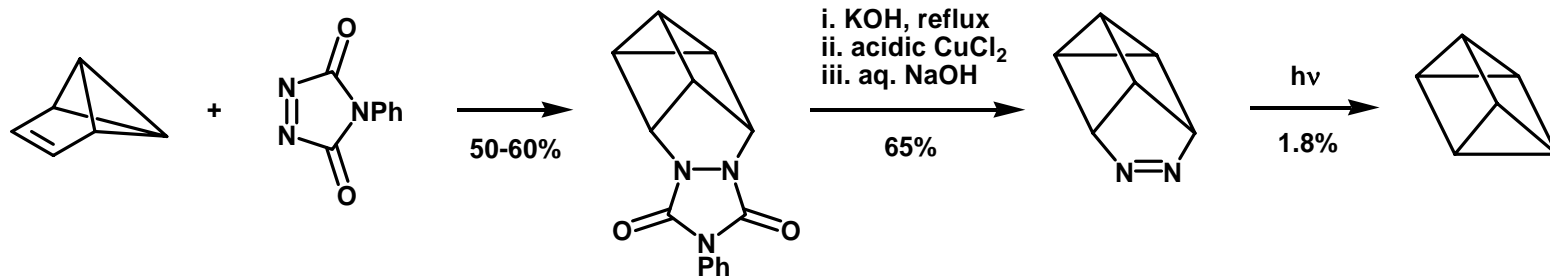


Spiroannellation of Enol Ethers of Cyclic 1,3-Diketones. A Simple Stereospecific Synthesis of β -Vetivone

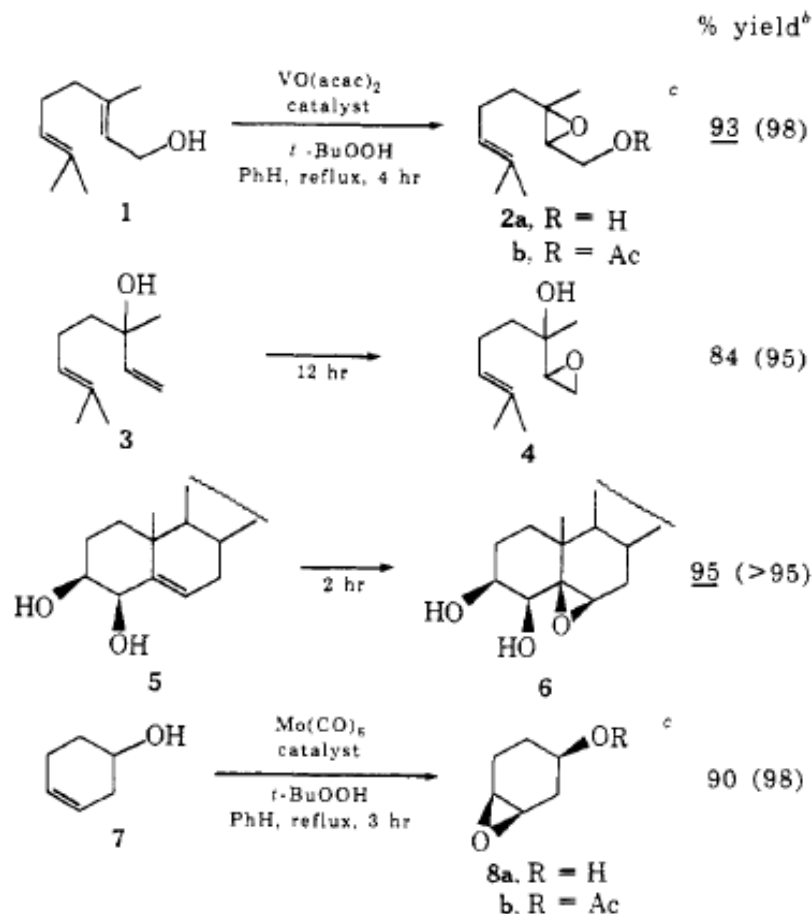
Application of the Stork-Danheiser alkylation:



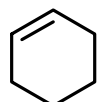
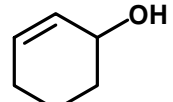
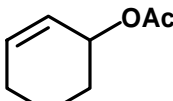
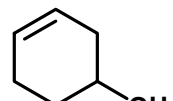
Synthesis of Prismane



High Stereo- and Regioselectivities in the Transition Metal Catalyzed Epoxidations of Olefinic Alcohols by *tert*-Butyl Hydroperoxide

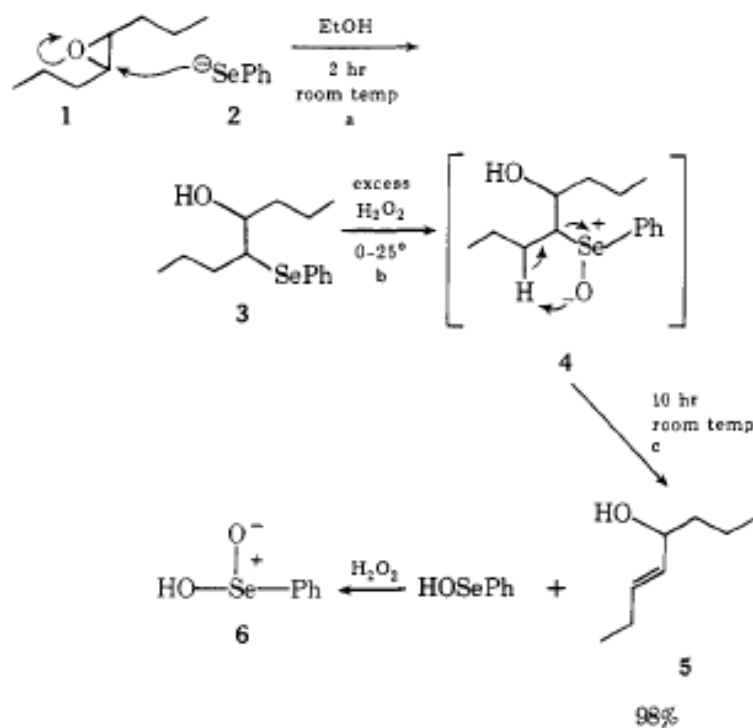


Relative Rates
(*syn:anti* diastereoselectivity)


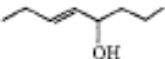

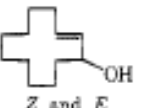

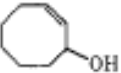
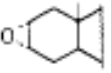
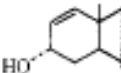
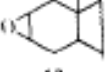
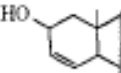

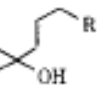








Olefin	Relative Rates (<i>syn:anti</i> diastereoselectivity)		
	Peracid	Mo(CO) ₆ <i>t</i> -BuOOH	VO(acac) ₂ <i>t</i> -BuOOH
	1.0	1.0	1.0
	0.55 (92:8)	4.5 (98:2)	>200 (98:2)
	0.046 (37:63)	0.07 (40:60)	
	0.42 (60:40)	11.0 (98:2)	10.0 (98:2)

^a These reactions were run on a medium scale using the stoichiometry described below in detail for the oxidation of geraniol (**1**).
^b Isolated yields are underlined, all others are by glc relative to internal standard. The figure in parentheses is the isomeric purity.
^c Epoxy alcohols **2a** and **8a** decomposed thermally upon attempted distillation or glc analysis and therefore were acetylated *in situ* (pyridine-acetic anhydride) to give epoxy acetates **2b** and **8b**.

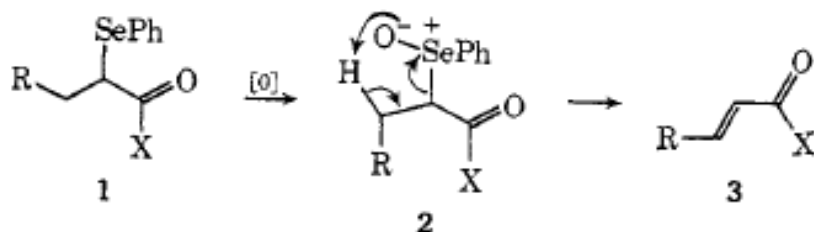
A Mild Procedure for the Conversion of Epoxides to Allylic Alcohols. The First Organoselenium Reagent



A Mild Procedure for the Conversion of Epoxides to Allylic Alcohols. The First Organoselenium Reagent

Epoxide ^{b, A}	Product ^A	Yield, ^c %	Solvent ^d	Step a time, hr (temp)	Step c time, hr (temp)*
		98	EtOH	2 (room temp)	12 (room temp)
		85	<i>n</i> -BuOH	16 (reflux)	1 (reflux)
 11		75	<i>n</i> -BuOH	16 (reflux)	4 (room temp)
 12		(40)	EtOH-THF 1:1	14 (reflux)	2.5 (reflux)
 13		(51)	EtOH-THF 1:1	8.5 (reflux)	4 (reflux)
					
8. R = 	7. R = 	95	EtOH	0.5 (reflux)	12 (room temp)
16. R = 	17. R = 	(79)	EtOH	2 (reflux)	2 (room temp)
10. R = 	9. R = 	(50)	EtOH	2 (reflux)	5 (room temp)
 14	 15	50	EtOH	0.5 (reflux)	0.1 (room temp)

Electrophilic and Nucleophilic Organoselenium Reagents. New Routes to α,β -Unsaturated Carbonyl Compounds



X = H, alkyl, alkoxy

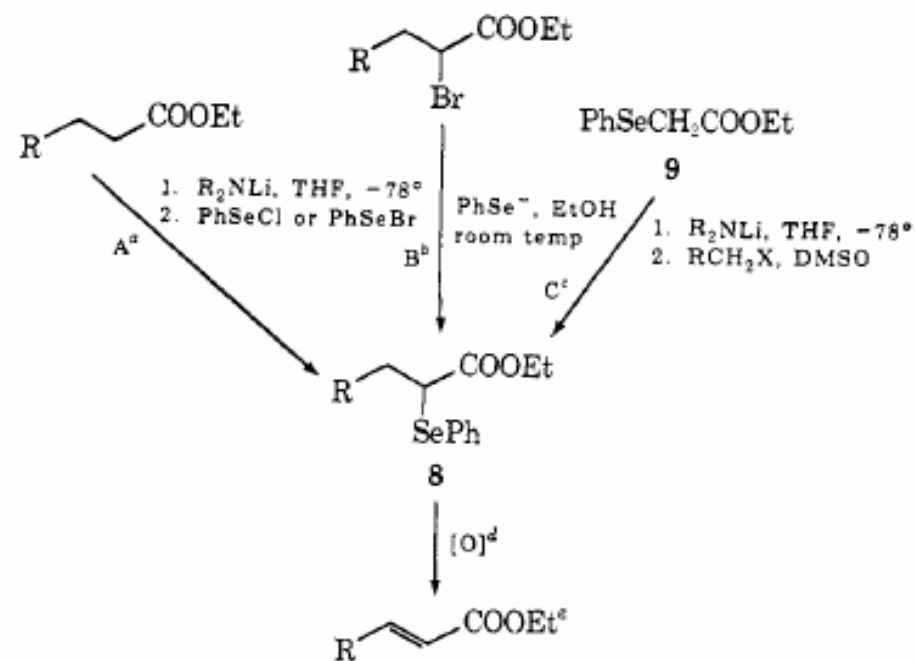


Table II. Unsaturated Esters Produced According to Scheme II

	Yield ^a of R-CH=CH-CO ₂ Et		
	Path A	Path B	Path C
R = Ph	80	78	65
R = CH ₃	83	89	60
R = <i>n</i> -C ₉ H ₁₉	79	82	

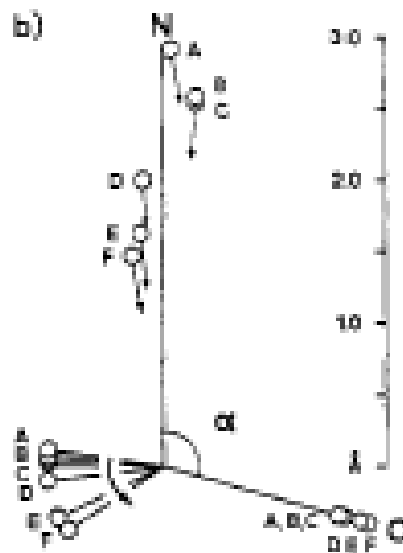
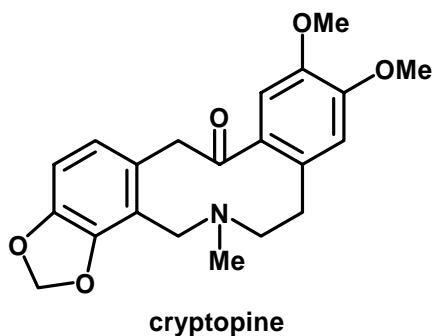
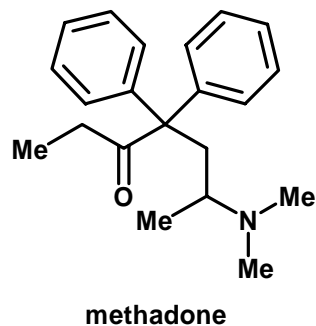
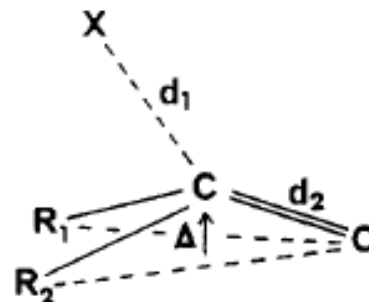
^a These are absolute yields determined by glc relative to internal standard.

Geometrical Reaction Coordinates.

II. Nucleophilic Addition to a Carbonyl Group

Crystallographic data from compounds containing R₂N: and C=O

compound	d ₁ , Å	d ₂ , Å	Δ, Å	N...C-O, deg
methadone	2.910	1.214	0.064	105.0
cryptopine	2.581	1.209	0.102	102.2
protopine	2.555	1.218	0.115	101.6
clivorine	1.993	1.258	0.213	110.2
retusamine	1.64	1.38	0.36	110.9
N-brosylmitomycin A	1.49	1.37	0.42	113.7



“As the nucleophile approaches the carbonyl C atom, the two alkyl substituents R and R' bend away and the C-O distance becomes slightly longer. The virtual constancy of α shows that the nucleophile approaches along a line. This line is not perpendicular to the C-O bond but forms an angle of about 107° with it.”

Generalized Frontier Orbitals of Alkenes and Dienes.

Regioselectivity in Diels-Alder Reactions

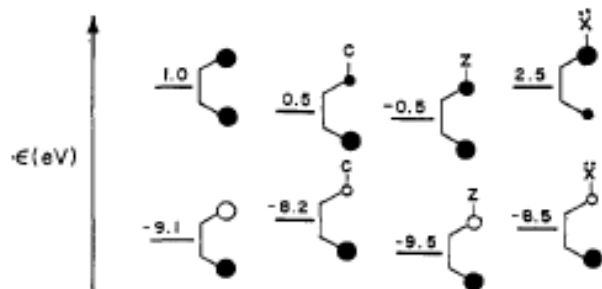


Figure 2. Frontier orbital energies and coefficients for 1-substituted dienes.

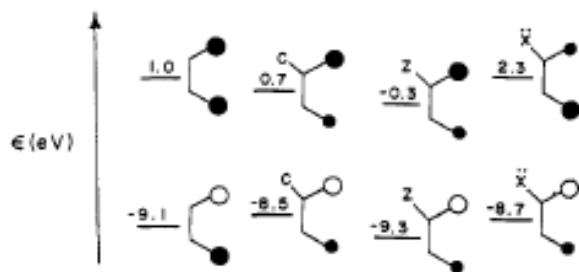


Figure 3. Frontier orbital energies and coefficients for 2-substituted dienes.

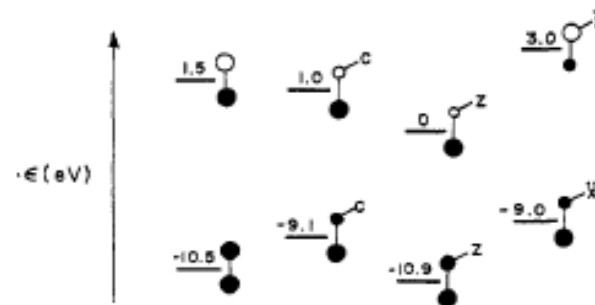
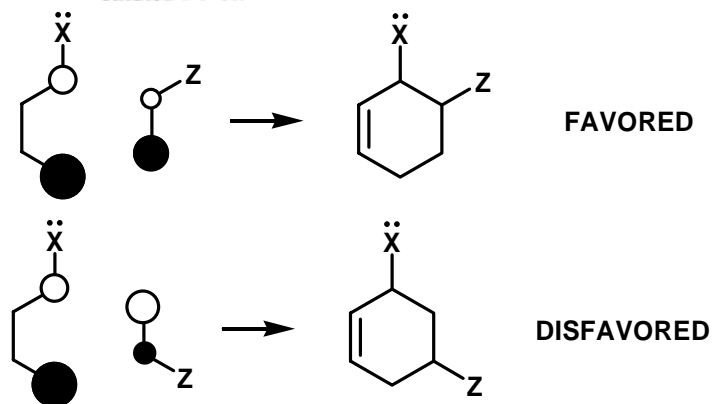
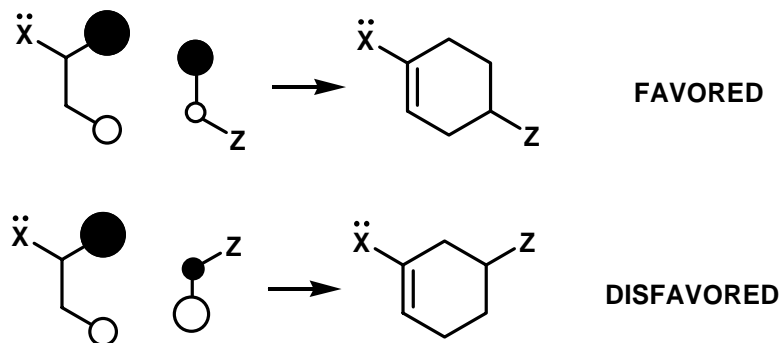


Figure 1. Frontier orbital energies and coefficients for dienophiles (C = CH_2CH_3 , Ph, etc.; Z = CHO, CN, etc.; X = R, OR, NR_2 , etc.)

C = conjugating substituent
Z = electron-withdrawing substituent
X = electron-donating substituent

Energies mostly from experiment. Relative orbital coefficients mostly calculated.



On Lewis Acid Catalysis of Diels-Alder Reactions

FMOs basically slightly perturbed butadiene orbitals

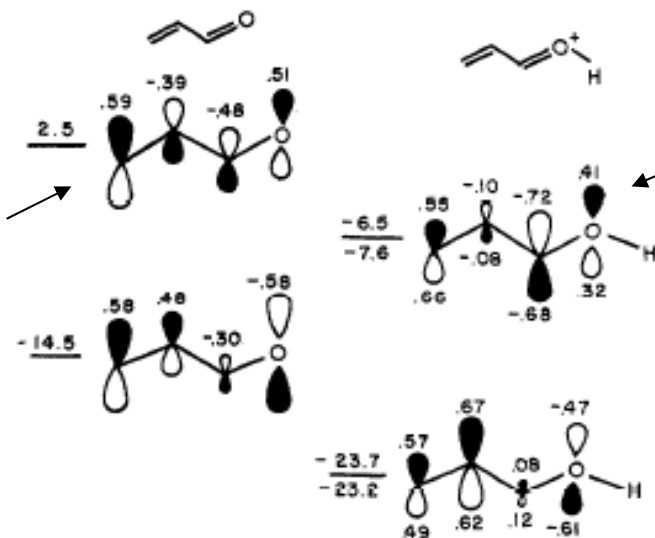


Figure 1. Frontier orbital energies (eV) and coefficients for acrolein and protonated acrolein.²

more like allyl cation

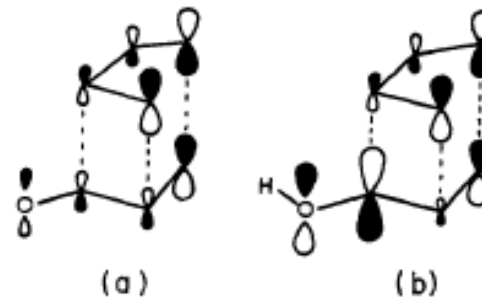


Figure 2. Diene HO-dienophile LU interactions in endo transition states with (a) acrolein and (b) protonated acrolein.

Benefits of Lewis acid complexation (for normal electron demand Diels-Alder)

- (1) Lowers the LUMO energy → increased reaction **rate**
- (2) Greater difference in LUMO coefficients at α and β carbons → increased **regioselectivity**
- (3) Greater secondary orbital overlap → increased **stereoselectivity** (endo:exo) and improved **asymmetric induction** with chiral dienophiles (b/c of “tighter” transition state)