TuTh 11

Summer → Nov 1964

streckperforerat

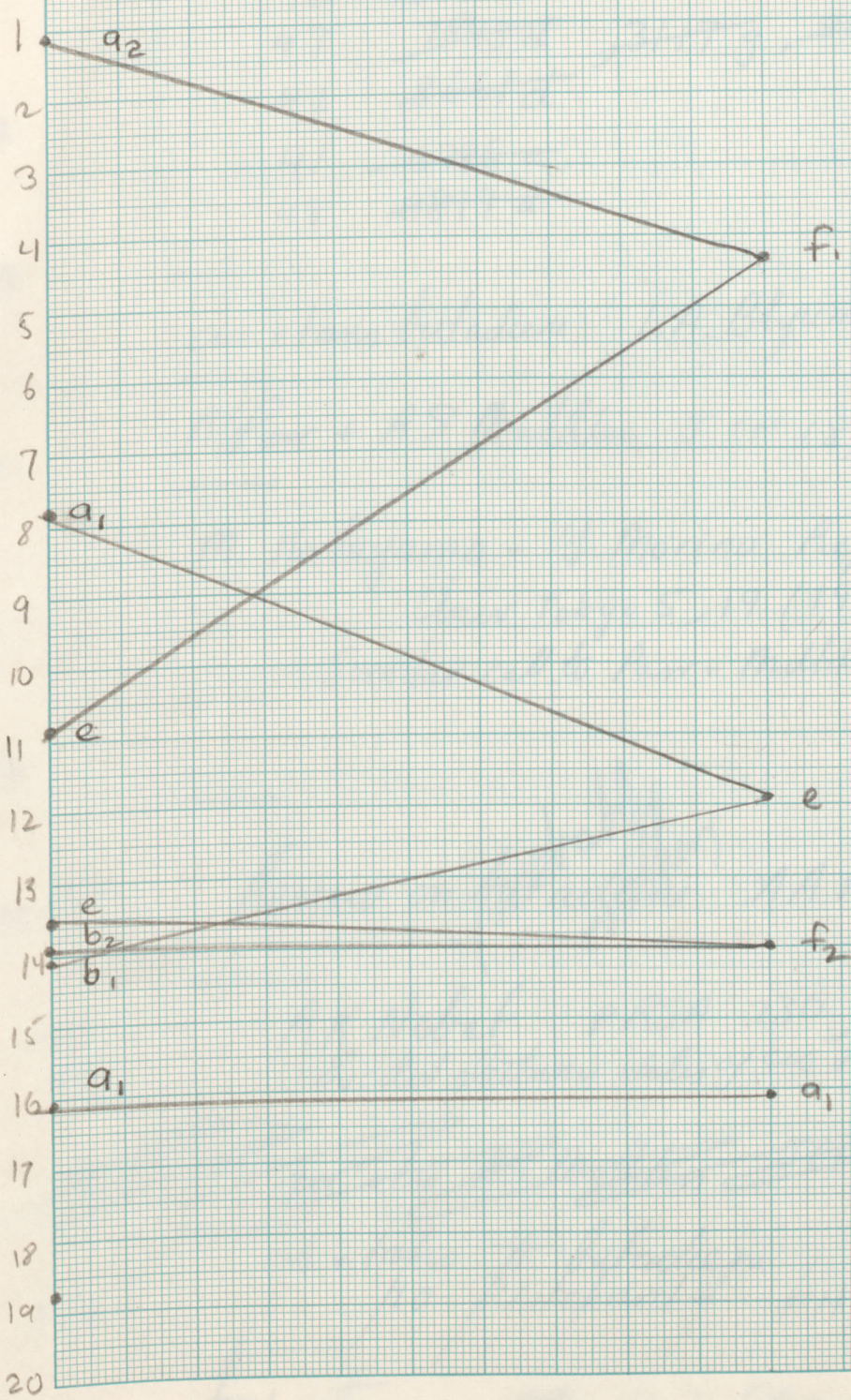
KOLLEGIEBLOCK

Roald Hoffmann

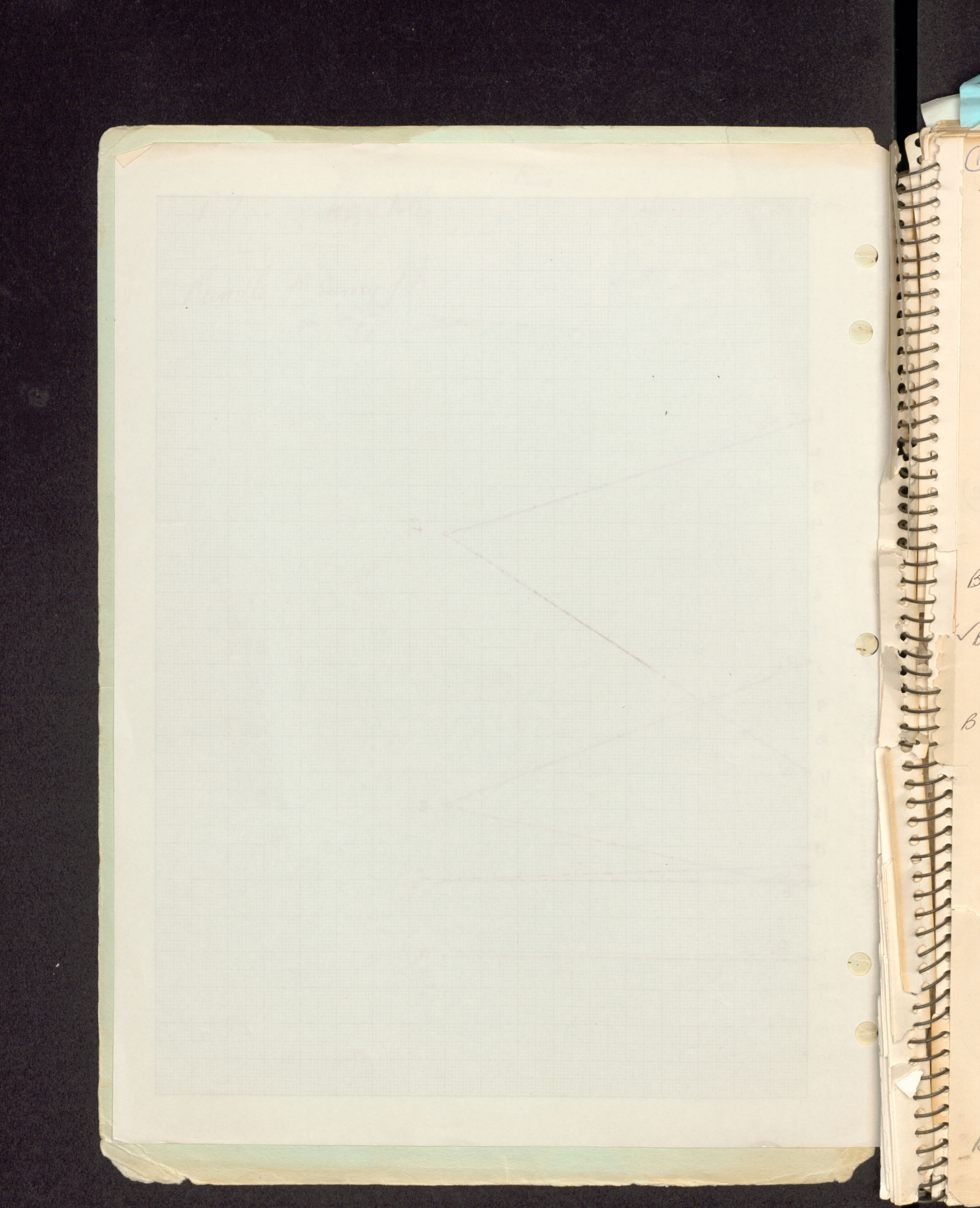
B7 $H_{rs} = NH_{rr}\, e^{-R_{rs}}$ but only used for π systems.

Rundle in "Survey of Progress in Chem" ed A F Scott
on SF_6 without d orbitals.

tetrakedrane
⇌ cyclobutadiene
(see earlier notebook)



10 X 10 TO THE CM. 358-14B
KEUFFEL & ESSER CO. MADE IN U.S.A.



(1)

BJ Spectrum WC Price, AD Walsh PRSA 174, 220 (1940)
trusting in draft by
EP Carr, LW Pickett, H. Stücklen
Rev Mod. Phys. 14, 260 (1942)

Butadiene

5th Dec.

44 ~~4330 i~~ ~~8177 h~~ ~~4298~~ g
45 ~~943 c~~
49 ~~14467 i~~
50 ~~12630 f~~ ~~5393 a~~
46 ~~9360 d~~ ~~1313 e~~
47 ~~7843 d~~ ~~3117 g~~, ~~8629 f~~
42 ~~8661 d~~
41 ~~6786 e~~
48 ~~9897 d~~

B1 cis + trans butadiene L.A. Blyumenfeld ~~PA~~ NAH 12,595 (1948)

B2 RG Parr + RS Mulliken JCP 18, 1338 (1950)

B3 M. Katayama + Y. Morino Rept. Inst Sci Technol. Univ. Tokyo 5, 19 (1951) CA 46, 1313e
Similar call to Parr + Mulliken.
cis-trans 0.79 ev !
barrier 2.54 ev !

B4 Review on butadiene probably nothing AA Petrov, Uspekhi 22, 905 (1953)

B5 RK Nebat PRSA 230, 322 (1955)
Excited electronic states of cis + trans butadiene.

B6 ~~see also RS Mulliken JCP 23, 2343 (1955)~~

B7 cis + trans 1,3 butadiene
HO Pritchard + FH Sumner, PRSA 235, 136 (1956)

B7a Structure D.J. Marais, N. Sheppard + B.P. Stoicheff, Tetrah. 17, 163 (1962)

(2)

51 ~~3944 f~~

52 ~~6896 e~~

53 ~~20961 i~~ ~~10717 g~~ ~~11981 g~~

54 ~~9482 e~~

55 ~~23160 e~~ ~~17207 b~~ ~~15370 c~~ ~~12035 a~~

56 ~~8538 e~~

57 ~~3258 g~~

58

59

√B15 R. S. Mulliken Rev Mod Phys ~~4~~ 14, 260 (1942)

JCP 30

B8 F L Pilar ~~JCP~~ ~~33~~ 375 (1959) 29, 1119

allylic type transition state in 1,3 butadiene reactions

B9 A. Almenningen, O. Bastiansen, M. Traetteberg

√ ACS 12, 1221 (1958)

electron diffr. structure trans. C=C 1.337

C-C 1.483

√√B10 Photochemistry R. Srinivasan JACS 82, 5063 (1960)

√~ B11 Cis vs trans chemical

WB Smith + J.L. Massingill JACS 83, 4301 (1961)

√√B12 I. Fischer-Hjalmars, Tetrah 19, 1805 (1963)

Tetrah 17, 235 (1962)

B13 ~~AC Longuet-Higgins + JN Murrell, Proc Phys Soc~~ 68, 601 (1955)

√√B14 JG Aston + G. Szasz JCP 14, 67 (1946)

thermodynamic

~ 4%

B12 ~~Sum of~~ Superposition of H-H repulsions

+ Conjugation energy

gives total curve

O (trans)	90	cis
-10.6	-0.2	-4.3
-11.1	-0.3	- 6.9
-10.5	-0.5	-2.4
-10.9	-0.6	-5.0

So my curve is different in that I have no activation energy for trans-cis interconversion. I think this is in agreement with the fact that ~~the~~ reactions such as the Diels-Alder proceed smoothly

---

B10 butadiene does not give cyclobutene at 2000-2500 Å irradiation → H_2, $HC\equiv CH$, $H_2C=CH_2$, CH_3CH_3, 1-butyne, 1,2 butadiene dimers

On $\pi \to \pi^*$ excitation you weaken ~~the~~ C=C & strengthen C–C. Yet C=C doesn't break. Well it loosens a little ..... to uncouple coplanarity.

B14 Evidence thermodynamic & chemical for presence
B11 of s-cis form in a few %. thermo 4 % chem 3,7 % pyr radical methylation

---

B1a D.R. Lide Jr. & M. Jen JCP 40, 252 (1964)
D.R. Lide JCP 37, 2074 (1962)

isoprene (fluoroprene = 2 ± butadiene on microwave.
Never, no as det.

B 2 SCF π system
rly on cis + transforms

π energy favors cis
core " " trans by slightly more

trans better by 0.12 ev

Mulliken B15 hedges
+ says it may be that in V_1 state
planar favors is still stable

$V_1 = {}^1B$

B5 Nesbet excited states cis - trans

(5)

Acrolein · Acrolein – Propenal

41
42 ~~4456 f~~ 51
52
43
44 ~~8181 g~~ 53
54 ~~1663 d~~ ~~2727 f~~
45
46 ~~2484 b~~ 55 ~~103 e~~ ✓ C=O
56 H
47 in excited state
48
49 ~~10063 c~~ 58 7386 g.
50 ✓✓ Ball Soc Chim Fr 1962, 1705 M. Bonnet 149 ° M. Lecordano

A1 FE Blacet J. Phys & Colloid Chem 52, 534 (1948)
Renewed) on photochemistry of aldehydes

A2 J.B. Bentley, K.B. Everard, R.J.B. Marsden, L.E. Sutton
J.C.S. 1949, 2957
dipole moment studies

A3 H. Mackle + LE Sutton
✓✓ TFS 47, 691 (1951)
electron diffr. cis/trans ratio 1:3 at 35°
not too good.

~~A4~~ Lamb 2. Electrochem 64, 135 (1960)
nothing to add Relaxation + conversion

✓ A5 K. Inuzuka BCSJ Jap 33, 678 (1960)
$n \rightarrow \pi^*$ spectrum analyzed, C=O stretch

A6 S. Nagakura Mol. Phys 3, 105 (1960)
intramolecular C–T spectra of acrolein
not relevant here, really

(6)

F. Bonnet + M. Coordano
Bull soc Chim. France 1962, 1705

trans + cis

method LCAO améliorée — dipole moment + transition

nothing re structure

Zimmerman re type II process
in Tetrahedron Suppl 2 2 393 (1962)

The bastard,

also HE Zimmerman + L. Craft.
Tetrah Let 1964, 2131 (1964)

re a paper re reaction of benzoquinone with tolan.

"However, thus far the evidence seems to ~~suggest~~ indicate σ delocalization to be less effective than π electron delocalization

he's putting us a down.

$n \rightarrow \pi^*$ more closely parallels alkoxyl radical than aryloxyl radical behavior ?

True: June 15 he hadn't heard my σ charge argument.

June 15
1964
reference
to that date

N. Hata + I. Tanaka JCP 36, 2072 (1962)

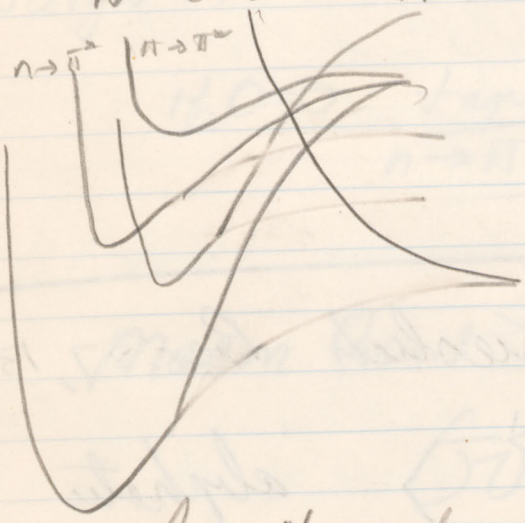
$n \to \pi^*$, $\pi \to \pi^*$ photolyses of pyridine N-oxide
& 2-Picoline-N-oxide

$n \to \pi^*$ ~ 30 KK 0-0 29.291
$\pi \to \pi^*$ ~ 36 KK

products H_2, O_2, CO_2, pyridine.

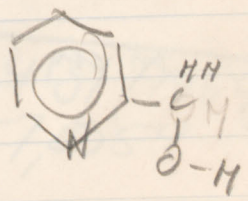
for irrad at 3261 Å yield of pyridine T dep
at 2537 not

from bond energies high λ light cannot dissociate
N→O bond ≈ 110 kcal (λ = 87.3



Read /// 2-picoline N oxide N. Hata. B.C.S.Jon 34, 1440 (1967)

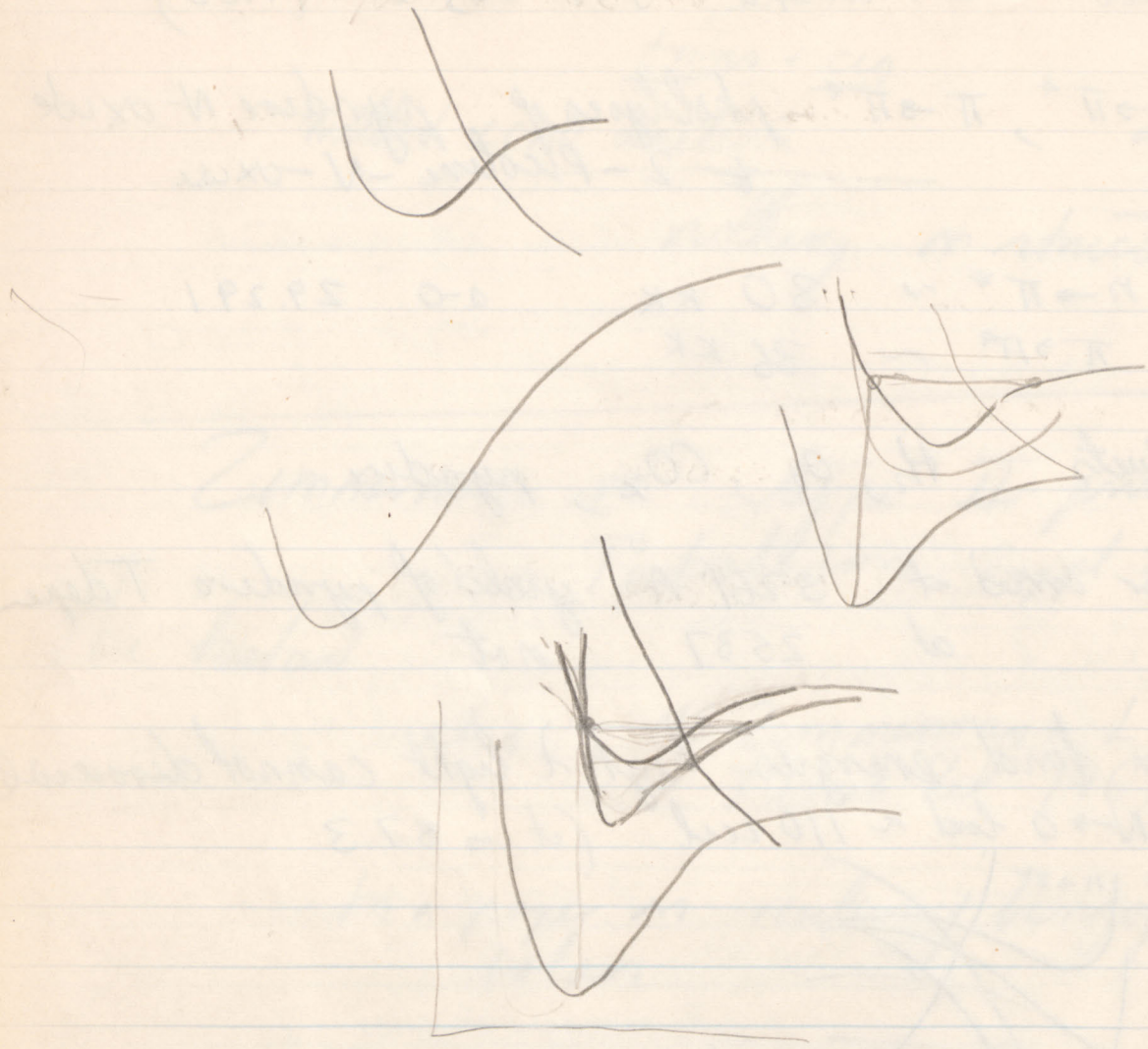
3261 → 2 pyridene methanol.



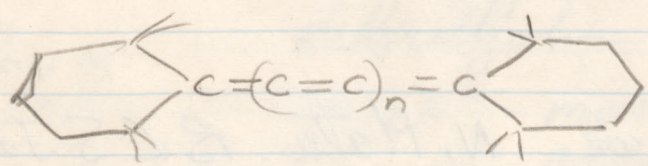
but at 2537 → 2 picoline

interesting.

Predissociation, to a repulsive state



F. Bohlmann & K. Kieslich Ber. 87, 1363 (1954)



alphatic

— 3,5,7,9 double bonds.

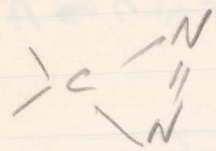
n = 4, 6, 8, 10

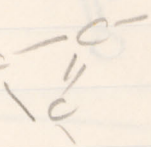
		in cm^{-1} intense	1st
maxima	4		271.5
	6	238	339
	8	284	400.5
	10	326	465

(9)

Diazirine UV spectra
A. Kan Spectrochim. Acta 20, 97 (1964)

Conclusion $\pi \rightarrow \pi^*$ 2900-3200 small f value



analogue of


diazomethane 2600 $\pi \rightarrow \pi^*$
3000-4000 $n \rightarrow \pi^*$

see also W.H. Graham JACS 84, 1063 (1962)

Georgio + Robinson JCP 31, 1678 (1958)

$H_2C{=}O$ triplet is also pyramidal
$n \rightarrow \pi^*$

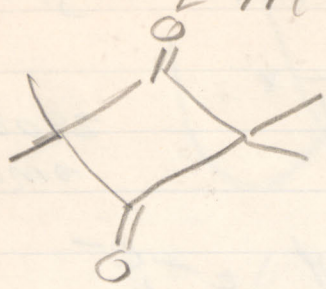
Mason Quart Rev. 15, 287 (1961)
Good Review on UV spectra

Glyoxal Braud TFS 50, 1131 (1954)
King JCS 1957, 5054

Bohlman + Keesluh ~~Ber.~~ 87, 1363 (1954)

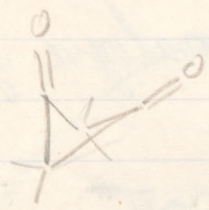
(10)

E M Kosower JCP 38, 2813 (1963)



3400 $n \rightarrow \pi_1^* + \pi_2^*$ A

3000 $n \rightarrow \pi_1^* - \pi_2^*$ B



do a calculation on this

3000 band has structure
3400 doesn't

V. G. Krishna & L. Goodman JCP 37, 912 (1962)

(σ, π^*) states mix into
(π, π^*) triplets
⊥ polarization

R. S. Berry JCP 38, 1934 (1963)

argues that once alkylated
monoolefins C-C bonds α to double bnds
are broken in 2537 Å irradiation

see J R Major, B. Nile, J. C. Robb
TFS 57, 1336 (1961)

F. L. Pilar JCP 29, 1119 (1958)
30, 375, 591 (1959)

1,2 vs 1,4 addition treated badly theoretically

Pedley TFS 57, 1492
58, 23

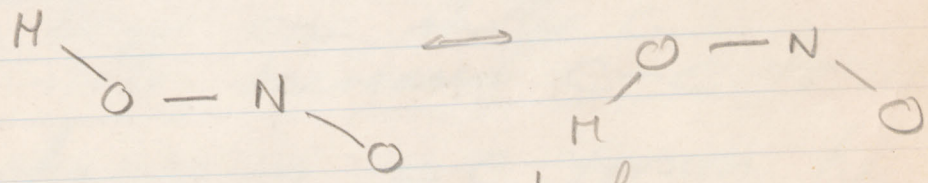
has Summons seen this

Mulliken formula for unbonded attr.

O. Sovers + W. Kauzmann JCP 38, 813 (1963)

trans more stable than cis ~.7 kcal.

HONO dimer



dimer ~10 kcal

R T Hall
+ G C Pimentel JCP 38, 1889 (1963)

(12)

Carbonium ions

J. Rosenbaum & MCR Symons Mol Phys 3, 205 (1960)
as PCS 1959, 92

R.S Berry JCP 26, 1660 (1957)
Butadiene π calculations

as below ions

≡ N⁺er

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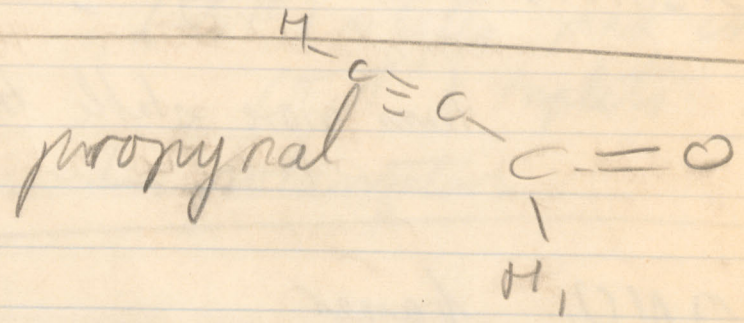
propynal



C-H, stretch 2858 ground
2952 excited

(13)

Butadiene propenal

5:30
4:30
20

✓ JCD Brand + DG Williamson
DFS 35, 184 (1963)

~ C–H ground
$n \to \pi^*$ 2800

4122 Å f

3865 → 2800 π
$n \to \pi^*$

✓ R. Wagner, J. Fine, JW Simmons + JH Goldstein
JCP 26, 634 (1957)

mw C–C 1.45 C–H 1.09
C=C 1.36 C=O 1.22
∠ C–C=C 122°5' = ∠ C–C=O ∠ C=C–H = 120°

✓ MS Debroot J. Kumb PRSA 242, 36 (1957)

$V = \frac{V_1}{2}(1-\cos\phi) + \frac{V_2}{2}(1-\cos 2\phi)$

4.96
2.06

$V_1 = 720$
$V_2 = 2080\ cm^{-1}$

Brand where does this come from?

trans		trans	
408.167	ground	406.575	1.592
405.307	$n \to \pi^*$	403.738	1.569
405.000	$\pi \to \pi^*$	405.496	−0.496

agreement on longer C=C shorter C–C in excited state, increased C–C torsion.

I get no change on =C torsion, he gets it decreased.

Propenal

Butadiene

Aston, Szasz, Wooley, Brickwedde JCP 14,67 (1946)

2.3 kcal cis-trans

R.G. Parr + R.S. Mulliken JCP 18,1345 (1950)

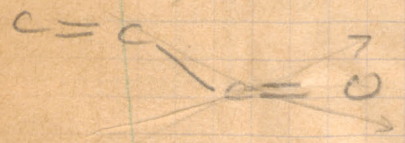
2.8 cis-trans only on butadiene

Electron diffr.

H. Mackle + L.E. Sutton JFS 47,691 (1951)

C=O 1.21 ± .02
C=C 1.36
C-C 1.46

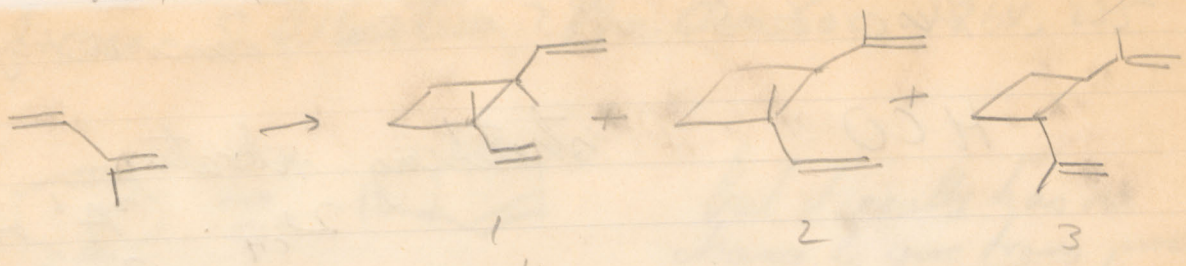
$\mu = 3.11$ 14° from C=O axis



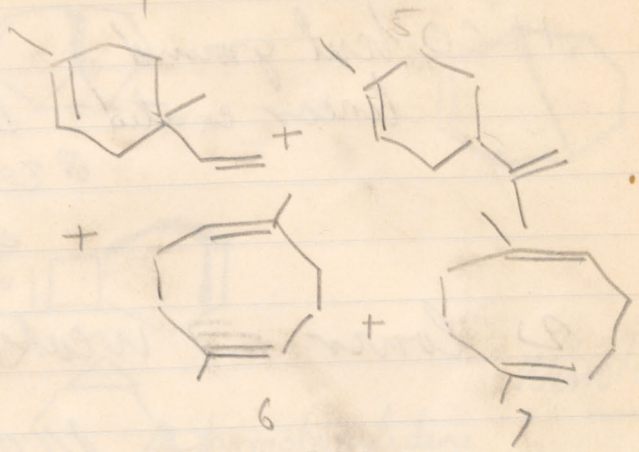
electronic energy favors cis by 0.85
core repulsion 0.97 favors trans

(15)

GSHammond + RSH Liu JACS 85, 477 (1963)



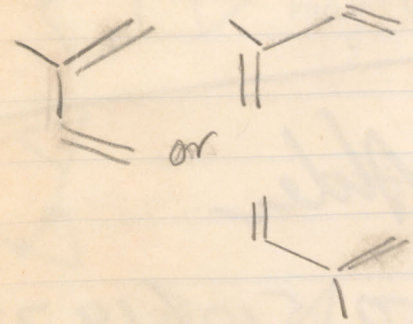
1 2 3



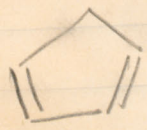
4 5 6 7

one precursor → 1, 2, 3, 6, 7

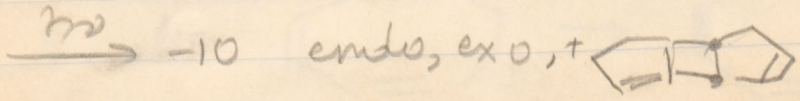
another → 4, 5



NJ Turro GS Hammond JACS 84, 284 (1962)



DA, 0° → endodihydrodicyclopentadiene



Disc. F.S. #35 p. 222 comment by Mills

HCO : stretching vibration

ν_{CH} $^2A'$ ~2700
$^2A''$ ~3300

HCO bent ground
linear excited D_e ground state = 33 kcal more than in excited state even though vibration lower

ν lower $\Rightarrow$ weaker bond

i.e D_e looks like in this case "stronger" bond is easier to break

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Stereochem. of Diels Alder

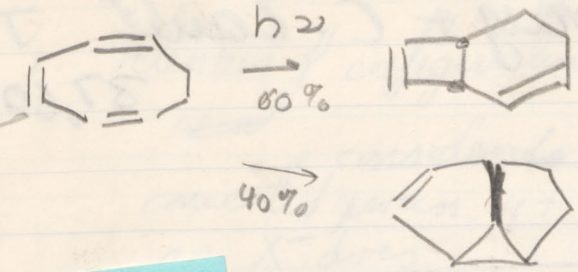
Alder Angew. Chem 50, 510 (1937)

Butz JOC 5, 171 (140)

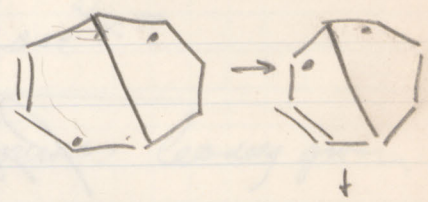
(17)

J. Zirner + S. Winstein Proc. Chem. Soc. 1964, 235

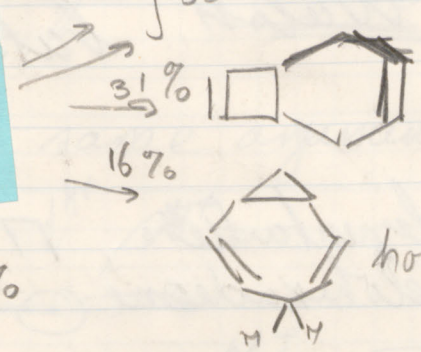
like Chapman? JAES July 5



but it really has no chance to give trans product



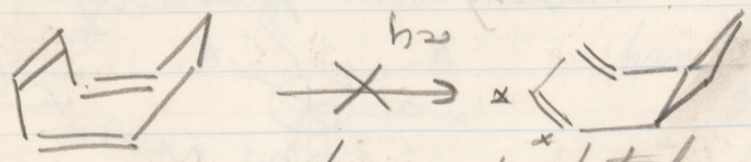
July 1964?



Winstein

"bis homobenzene"

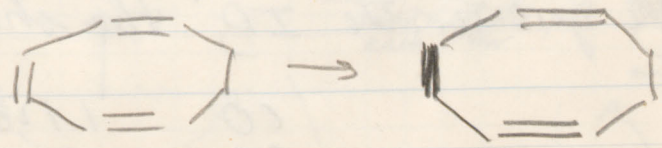
maybe



because 1. photochemical reaction wants different stereochemistry

2. H's at x—x are not coplanar at left

Chapman finds also



d orbitals in SF_6

see DP Craig + C. Zauli JCP
37, 601, 609 (1962)

Price + Walsh butadiene
PRS A 174, 220 (1940)

cyclopentadiene 179, 201 (1941)
cyclohexadiene

can't really tell if vibr. progr. in butadiene
but not in cyclopentadiene. No
mention of possibility of non planarity in butadiene
N → V,

Bowden – Walsh TFS 41, 498 (1945)
nothing about planarity

done paper on CO₂

A. D. Walsh TFS 42, 56 (1946)
correlates for carbonyl compounds
ionization potentials + bond length
the greater the IP, the shorter the bond.

CO	1.128	14.1
CO_2	1.15	13.73
H_2CO	1.21	10.83

he correlates it to negative character of O increasing

or $>C=O \longrightarrow >\overset{+}{C}-O^-$ resonance
but this involves π electrons
but IP is for σ

trans elimination

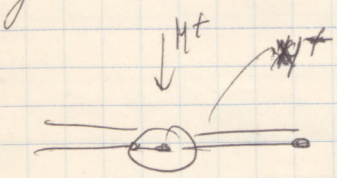
$CH_3CH_2X \rightarrow$ ~~X~~$^-$ + $CH_3CH_2^+$

1. retention of configuration i.e

~~i.e~~ i.e considered as concerted process. H+ begins to leave as X^- does

2. trans effect in $\underline{CH_3CH_2^+}$ determines leaving group

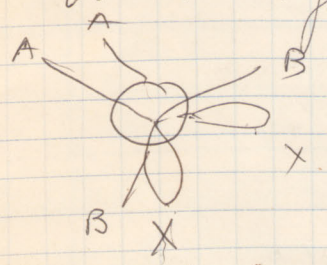
Can we give same argument for trans addition

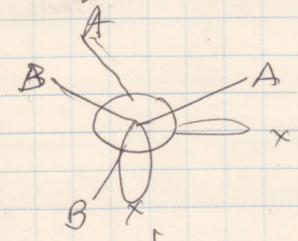


trouble how to define effects felt most at transposition :- Try an approach of an X^- from various sites.

Idea via Bunnett

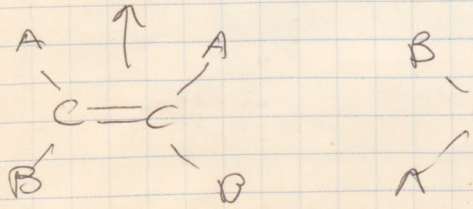
Walsh : fits better with cis pair

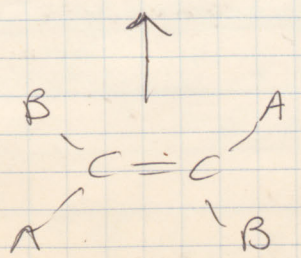




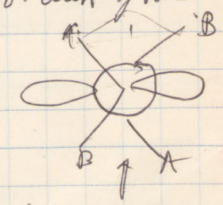
d, l
rac.

meso

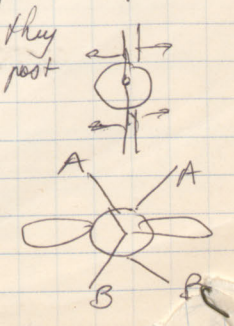




have to assume it gets to this form by rotation from



what happens when A + B so large they cannot rotate past each other



But does one get trans addition in some compounds where transition has no freedom of rotation at all.

JCD Brand – glyoxal. $A_g \rightarrow A_u$ vibrational analysis

TFS 50, 431 (1954)
3700 → 4500

AD Walsh TFS 42, 66 (1946) UV spectrum
nothing much

RS Mulliken JCP 3, 564 (1935)
mentions possibility of delocalization in H_2CO (but really doesn't think it's very important)

RS Mulliken JCP 3, 517 (1935)
makes π orbitals on ethylene 1 → 2 ev below π
says excited orbitals of CH_4 + CH_3CH_3 are Rydbergs.

also HL McMurry JCP 9, 231 (1941)
esp. footnote 35a

HL McMurry JCP 9, 241 (1941)
looks at glyoxal + says onset of n is small + near degeneracy results

Sensitivity of I.P. to substitution?
formaldehyde 10.2
acetone 10.9

Brand

— b_g
— a_u — — a_g b_u
— b_g
— a_u

assigns transition as $a_g \rightarrow a_u$ ($^1A_g \rightarrow {}^1A_u$)

5200 Å "system" looks "allowed" ∴ not $b_u \rightarrow a_g$
= ($^1A_g \rightarrow {}^1B_g$)

ν_{trans} 232 excited
127 ground

barnes 3.2 in ground kcal /
in hormone 10-8 in excited
oscillator approx on, as assumed minimum

E. Eastwood + C. P. Snow, PRSA 149, 446 (1935)

C=O absorption band ~ 2900 diagnostic
of ketones + aldehydes position + shape.

already mentioned that $n \rightarrow \pi^*$ transition involved
in α bond cleavage noted, since it would
affect C-H bonding to some extent
" " PRSA 149, 434 (1935)

in summary "The transition is not localized in the
double bond, and will affect the atoms adjacent
to the C atom of the double bond" (their italics)

(22)

ARM Cole + H.W. Thompson PRSA 200, 10 (1949)
analysis of vibration-rotation bands
string evidence = bars

G W Keng JCS 1957, 5054 ff

	cc+co	∠ CCO
gwung	2.726 ± 0.062	121.9 ± 1.3
exc	2.742	125.0

approx. bond length

	C–C	C–O
gr	1.50	1.22
exc	1.53	1.19

± .1

A. July + J.C. Donadini LCAO améliorée
cis + trans glyoxal
spectra only.

Still look at
~~Tanaka Bull Soc Chem Jpn 70, 110 (1961)~~
~~Ebsworth J Mol Spec 6, 483 (1961)~~
~~Kotoyama Bul Chem Soc Jpn 26, 239 (1953)~~
M. Kotoyama

Structure C–O 1.20
C–C 1.47
∠HCC 114 ass
∠CCO 123 ass
C–H 1.09 ass

JE Lu Valk + V. Schomaker
electron diff JACS
61, 3520 (1939)

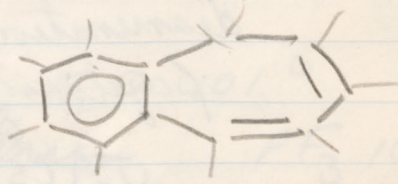
(23)

On σ + π overlapping

CA Coulson + R Taylor PPS 65, 815 (1952)
↑ most direct

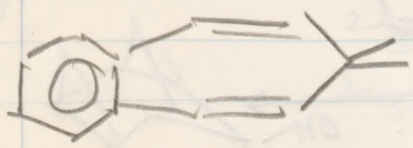
see also CA Coulson, P.W. Higgs, NH March
Nature 168, 1039 (1951)
Altmann S.L. PRSA 210, 327, 343 (1952)

Benzocycloheptene;

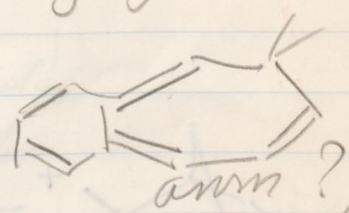


Bull Soc. Chim 5, 848 (1968)

$C_{11}H_{10}$
Cycloheptabenzene
Benzocycloheptene



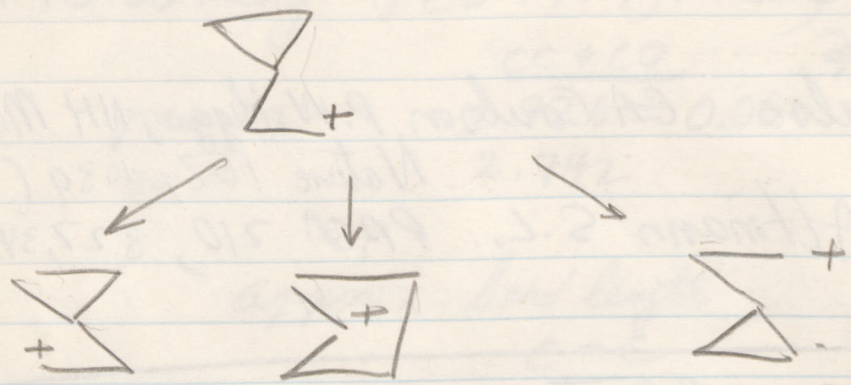
Ann. 369, 297 (1909)



JACS 73, 2239 (1951)

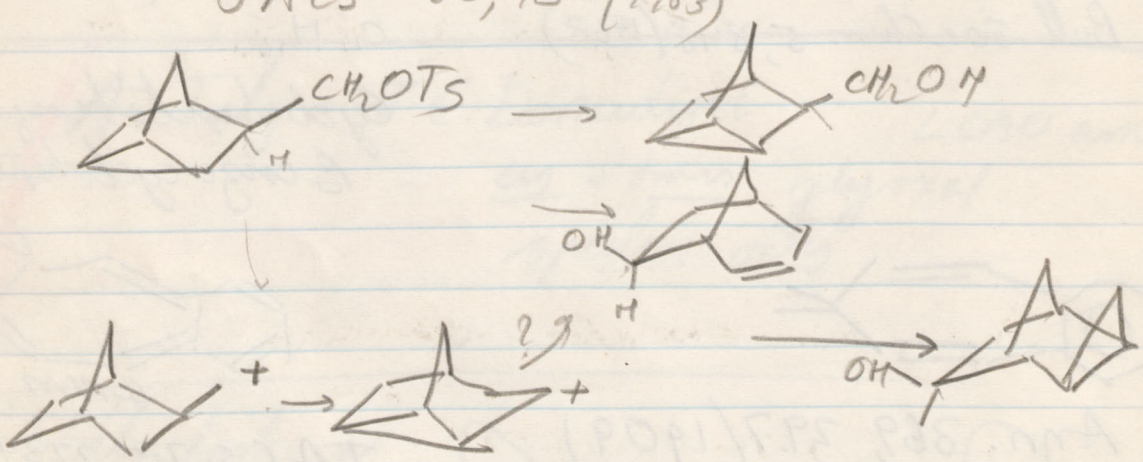
R P Sauers + J A Beesley Tetrah Let 2181 1964

Interactions of cyclopropyl groups with β carbonium ion.



bicyclo [3.1.0] hexyl

deamination of
cyclopropylethyl amine
Carter + Bunce
JACS 85, 932 (1963)



CH_3^+ Bartlett + Knox JACS 61, 3184 (1939)

25

Review on ketonization
Charpentier, Rivière, Skrobek + Tchoubar
Bull Soc. Chim France 1960, 1444
?

Formaldehyde

AO Walsh JCS 1953, 2260,
2266
2288, 2296, 2301, 2306
2318, 2321, 2325, 2330

(1) Nothing on FHF angles F_2O 101°
(2) Says excited acetylene non linear PF_3 104
Says nothing on cis or trans PH_3 93°50'

$H-C=O$ ν_2 = CO stretch
ν_6 = out of plane bend.
ν_5 = in plane deformation

Brand JCP 19, 377

Theory
Donor-acceptor

Phys. Chem
Ausloos $\Delta^+ H^+$ ACS Meeting Joyce Kaufman
on Div. of Fluor. Chem
DN Org: Effective Size of Fatom

Org. Chem: Zimmerman
Jaffe YH
W. A. Sheppard Fluorine color

Cage like Compounds

(26)

ACS Spring 65 Detroit — Fall 65 Atlantic City

Structure of Inorganic complexes.

Free Radicals (Readings (mostly)

Physical Organic (mostly)

Aromatic Char. + Resonance Theory (mostly)

Structures of Electronically Exc. Molecules (Ramsay)

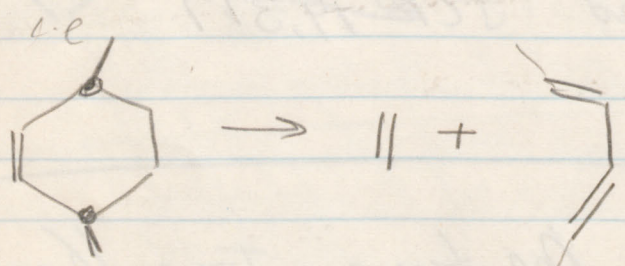
Quantum Chem (Hirschfelder (mostly

Diels-Alder Reversed 400 → 850°

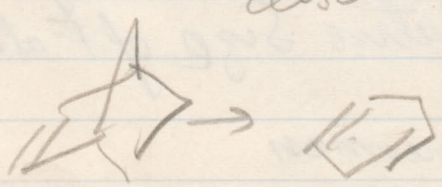
Uchimaya et al. JPC 68, 1878 (19

support for cyclic transition state

can one study stereochem of photochemical reversal of D.A.



also Hemden et al. JPC 68, 2016 (1964



300 → 400

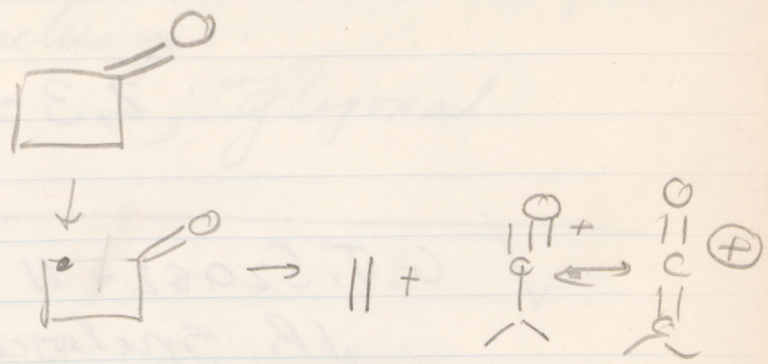
Doering

Stigmatropic r. Diels Alder

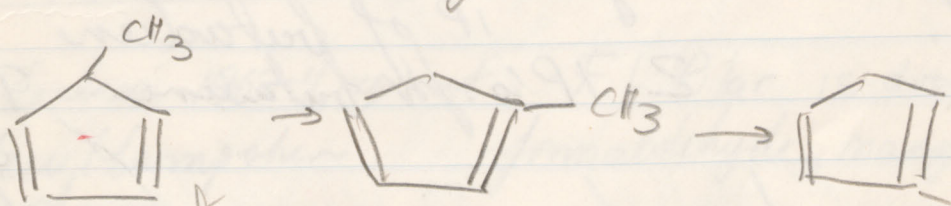
(27)

H J Hofman. Tetrah. Let 1964, 2329 (1964)

mass spec of



S. McLean + P. Haynes, Tetrah. Let 34, 2385 (1964)

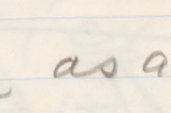


this → 1,2 H shifts but does not see any 1,3 ?

Mironov Tetrah 19, 1939 (1963)

Roth Tetrah. Let 17, 1009 (1964)

Allenger + Miller JACS 86, 2811

P+P calcn  as a fn of dih ∠

	N → V, λ.	f
0	230	0.456
90	182	0
180	212 mμ	0.997

cis ≈ trans 10 kcal barrier

calcd. for	bicyclic conj dienes
hexadiene	17
7	52
8	64
9	?

✓ H. Wynberg, A. DeGroot, D. W. Davies
Tetrah Let 1963, 1083

2,3-dc-t-butylbutadiene.

✓ G. J. Szasz + N. Sheppard TFS 49, 388 (1953)
IR spectroscopic study of the conformers of some chlorinated butadienes
mostly trans

✓ J M Sugden + A D Walsh
IP of butadiene
2 IP's. for butadiene: 9.02 trans
8.71 as
based on
cl. impact
funny because spect. el. impacts
9.3
comade in cis at 8.7
but are diffuse trans.

✓ Albright + Nelson JCP 26, 370 (1957)
perfluorobutadiene: can't conclude
of its cis, trans or enlem.

✓ Acetaldehyde KK Innes
+ LE Geddings
J Mol. Spec 7, 435 (1961)
doublet probably rotational; CO increase

✓ W H Eberhardt + H. Renner J mol Spec 6, 483 (1961)

no particular conclusions
I can see ; ~~g~~ glyoxal.

see G W Robinson on H$_2$CO Can J Chem 36, 31 (1988)

Coulson 1963-4 report F. L. Pilar is doing
U. New Hampshire formaldehyde, many configur.
Durham

See McWeeny + Ohn PRSA 255, 367 (1960)

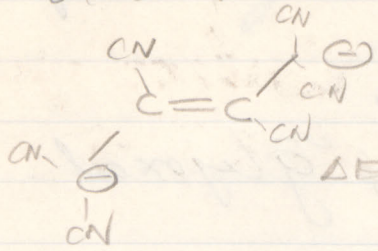
repeated Shull + Ellison $E = (\frac{eV}{})$

+ SCF	105	109.5	120°
	2061.0	2061.3	2061.9
bond orbital	2060.4	2010.4	2060.0
modified pair	2061.3	2061.2	2060.8

(30)

O.W. Webster JACS 86, 2898 (1964)

✓ abd to butadiene paper (—2)



interconvertible, isolatable

Is transition to my calculated C_2H_2 forbidden (how?)

Ingold + King 5 papers JCS 2708 (1953)

Read Can J Chem vol 36 begin

quote Mulliken 36, 10 (1958) on acetylene

he says cis

CH stretch ~~over~~

$^1A_1$ 2780 — $^1A_2$ 2851

see Brand J C S 1956

is ~~alkylene~~

(31)

On electron donor character of CH_3
see S. Basu in Coulson repts
JCP 30, 314 (1959) 1956-57

✓ In Steric effects in Conj. Systems
ed. GW Gray
Butterworths 1958

p. 73 ES Waight & R.L. Erskine
"Absorption Spectra of Conjugated
Carbonyl Compounds

shift → blue hypsochromic
hindered conj. ketones
Braude JCS 1949, 1890 ✓
Progress in Stereochem vol 1
Experentia 11, 457 (1955)

✓ also see Mumell JCS 1956, 3779

✓ See K Nisa J Pharm Soc Jap. 8, 630 (1953)

✓ Heilbronner - Gerdil Helv. Chim Acta
39, 1996 (1956)

timothy grass + birch

on butadiene what is f(osc. str) as a
function of dist.

CA Coulson, NH March + SL Altmann
PNAS 38, 372 (1952)

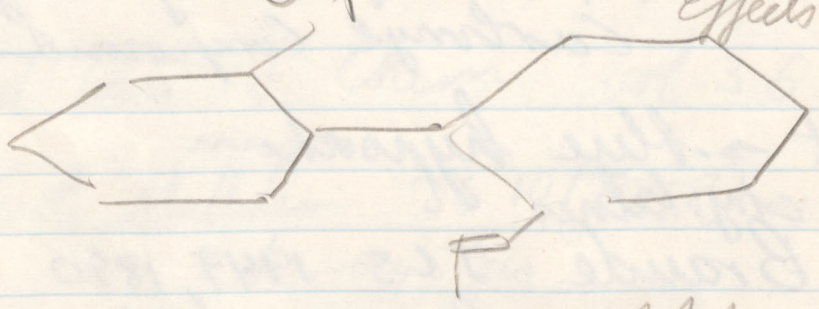
π electrons + σ electrons

Calculate σ + π distrb in benzene

1. mo
2. Thomas Fermi density in center

π electrons submerged in sea
cannot be separated

Have to try



see discussion in Steric Effects in Conj. systems p. 170 ff

$C_{12}F_2H_8$ = 64 orbitals

cis → trans

0 45 90 135 180

---

add note to Waight + Erskine in prepared paper.

Doering

(33)

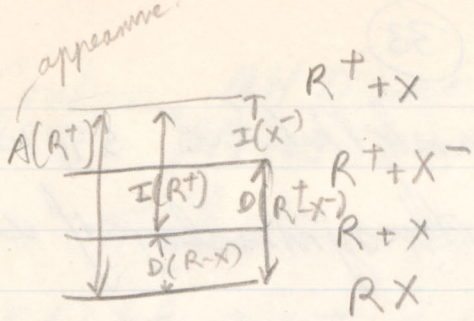
✓ N. V. Cohan Proc Camb Phil Soc 54, 28 (1958)
Spherical harmonics with symmetry of icosah. group

✓ ↑ TFS 59, 1695 (1963)
D. A Hutchinson Butadiene vs the cm

methylene + + allyl radical
methylene radical + allyl cation

calc bond lengths by diverse L-H + Salem

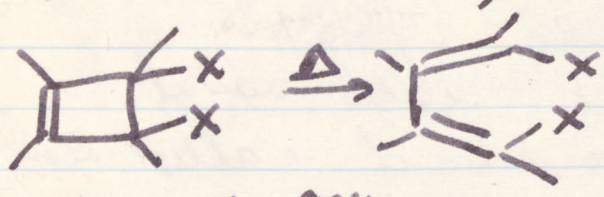
butadiene	1.344	1.484
+ cm	1.392	1.425



$D(R-X) = A(R^+) - I(R^+)$

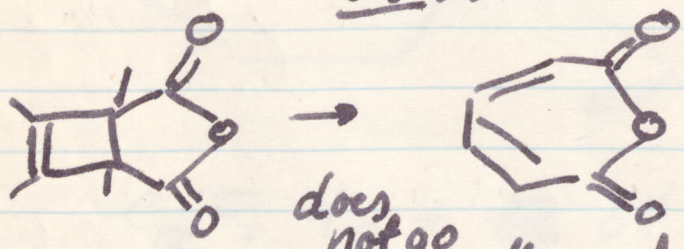
$D(R^+-X^-) = A(R^+) - I(X^-)$

W. Adam. Ber. 97, 1811 (1964)



X = H, OCH_3, Cl, OAc, Br, CO_2CH_3, I, OH, CO_2H

cis others unknown conf.

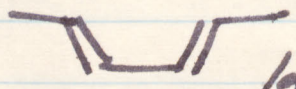


→ does not go thermally; but it goes photochem reverse

Fonken C+I 1961, 1575

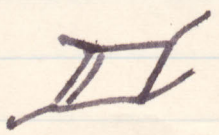
I_h cis → trans trans.

apparently thermal reaction here yields trans-trans



for I_h? i.e. X = CO_2CH_3

But R. Criegee + K. Noll Ann 627, 1 (1959) found opposite



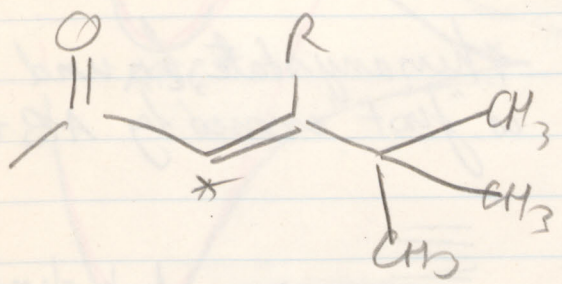
Δ → cis-trans

(35)

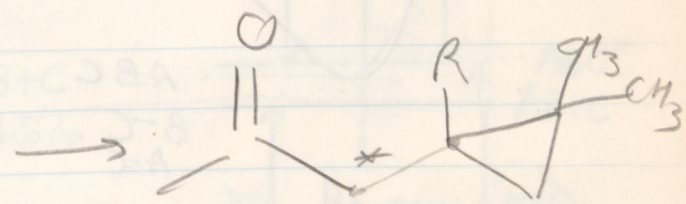
M. Yamatera
J. Inst. Polytech Osaka City Univ 5, 163 (1956)
supposed to use W-H.

RF Fenske + CC Sweeney IC 3, 1105 (1964)

M J Jorgenson + NC Yang
JACS 85, 1698 (1963)



R = H, CH_3



involves H transfer to *
(via O? + keto-enol?)

RS Tolberg + JN Pitts Jr, JACS 80, 1304 (1958)

at 3130° main reaction
= cis-trans isom.

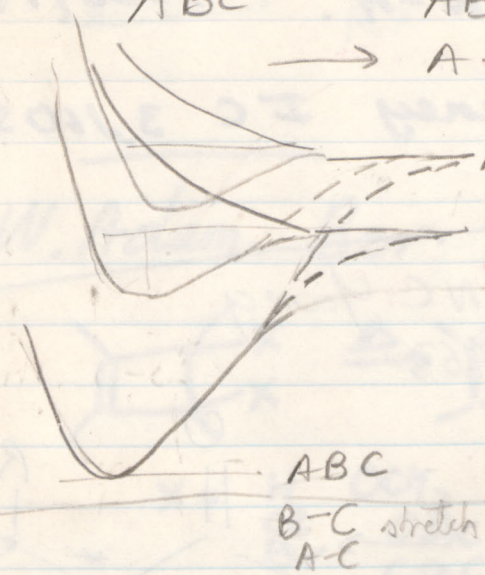
→ CO C_4H_8 C_3H_6 + CH_4.

no isomerization apparently

Klemperer argument

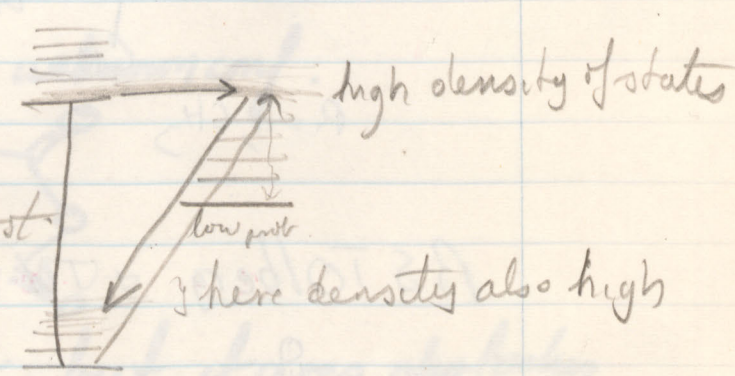
$ABC \longrightarrow AB + C \Rightarrow$ B C bond

$\longrightarrow A + BC \Rightarrow$ A B bond broken

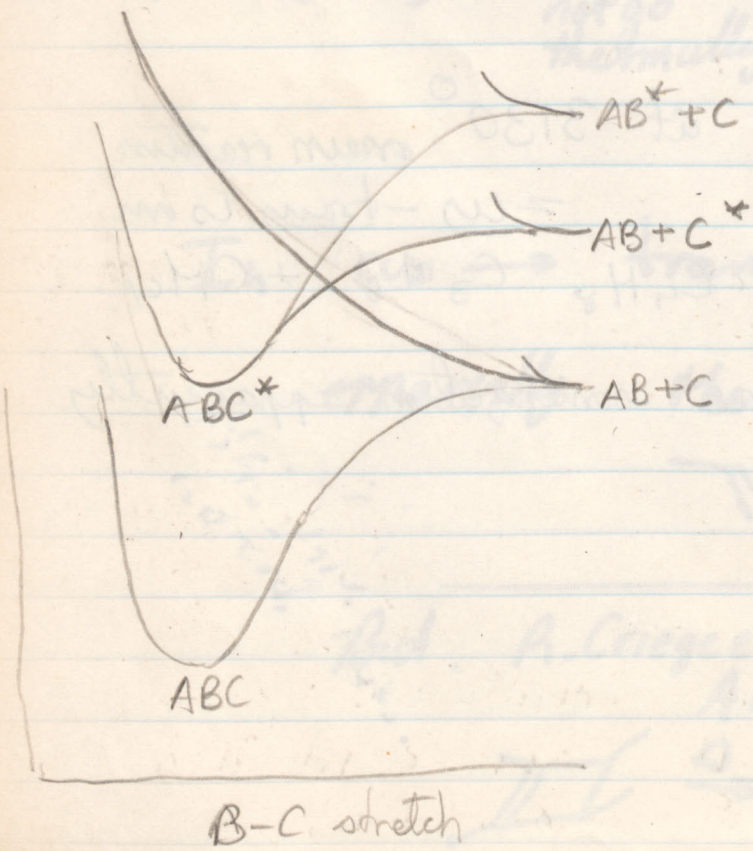


implies BC bond weaker than AB.

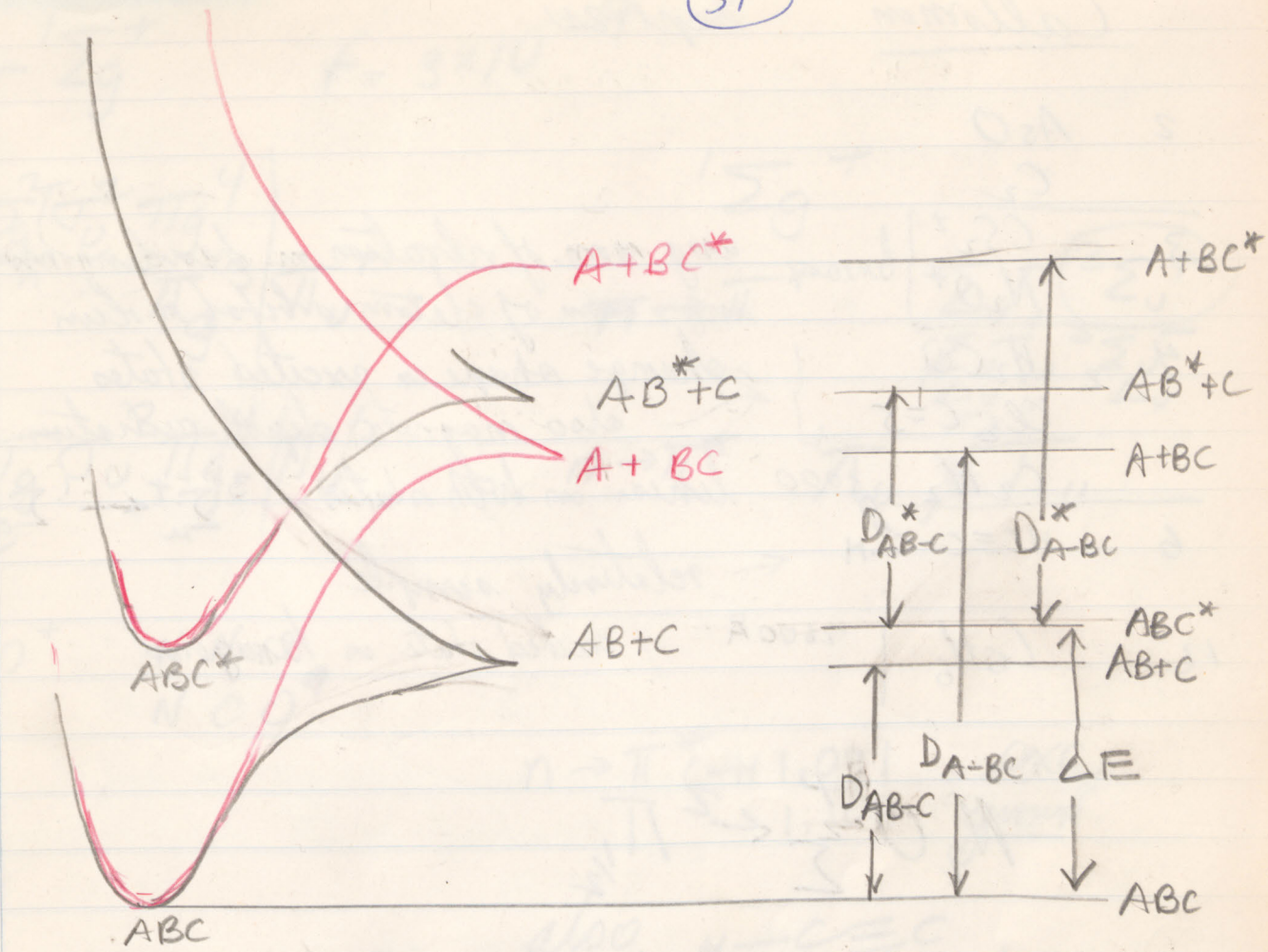
Then any state bound is "lost" crossed by AB+C



But my argument is not that the weakest bond breaks first in the excited state, but the bond which is weakened most



for simplicity consider only dissoc → $AB^* + C$



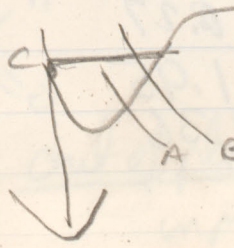
B—C →

A—B →

D_{AB-C} may be $\lessgtr$ D_{AB-C^*}

My criterion is that: compare $(D_{AB-C} - D_{AB-C^*})$ with $(D_{A-BC} - D_{A-BC^*})$. the one with the largest difference i.e, the most bond weakening will be most likely to break.

If transition probability (to a dissociative state) is a function of how far above the crossing one is, it seems clear that weakest bond will break.



Assumes that if we excite to C by a vertical transition, one will be more likely to get into curve A than B.

Sept. 24, 1964

(38)

Calloman Sept 24

2 AsO

C_2

3 CS_2^+ } linear ang mom. of vibration in bending modes } Renner type
N_2O^+ } ang. mom of electron orbital in plane

4 H_2CO } ← change shape in excited states
$Cl_2C{=}S$ } ← also magnetic dipole radiation spectra

C_2N_2 3000 linear in both states $^3\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$

6 $HC{\equiv}C{-}C(=O){-}H$ ← relatively simple

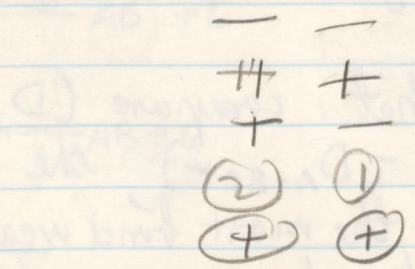
12 C_6H_6 | 2600Å excited state is hexagonal

$N_2O\ {}^2\Sigma^+ \leftarrow {}^2\Pi_{1/2}$

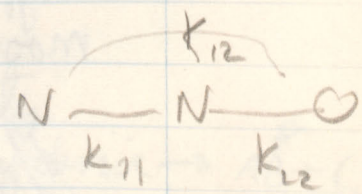
$\nu_1 = 1285$ N_2O

1126 N_2O^+ first electron away loosens

1345 " 2nd electron



N_2O^+ B' B'' N_2O^{18}



$\times 10^5$ d/cm

		r_{NN}	r_{NO}	K_{11}	K_{22}	K_{12}
N_2O^+	$B^2\Sigma$	1.140	1.141	17.82	15.12	−0.27
N_2O^+	$X^2\Pi$	1.155	1.185	11.80	8.25	+1.95
N_2O		1.129	1.188	17.88	11.39	+1.36

C_2N_2

$^3\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ $\quad f = 3\times10^{-9}$

$\sigma_g^2\sigma_u^2\pi_g^4\pi_g^3 \,|\, \pi_u'$

$\sigma_g\sigma_u^2\pi_g^4 \,|\, \pi_u'$

$^1\Sigma_g^+$

$\pi \rightarrow \pi^*$ $\quad {}^1\Sigma_u^+, {}^3\Sigma_u^+, {}^1\Sigma_u^-, {}^3\Sigma_u^-, {}^1\Delta_u, {}^3\Delta_u$

$n \rightarrow \pi^*$ $\quad {}^1\Pi_u, {}^3\Pi_u$

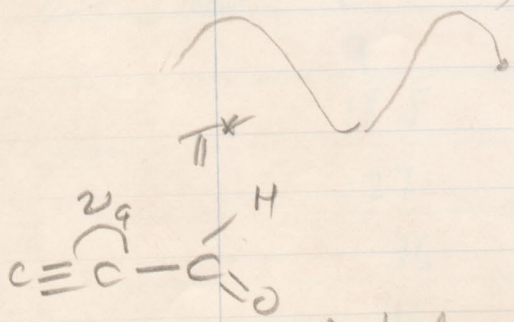
N_2O^+ $\quad NNO$
$\quad\quad NCO^+$

$n \rightarrow \pi^*$ $\quad C{-}H$ $\quad 1.091$ $\quad$ exc
$\quad\quad\quad\quad\quad\quad 1.106$ $\quad$ ground

also $H{-}C{\equiv}C$
changes from

$C{=}O$ $\quad 1.215$ ground $\quad 1.055$ ground
$\rightarrow 1.325$ exc. $\quad\quad 1.073$ exc.

	$C{\equiv}C$	$C{-}C$	$C{=}O$
ground	1.209	1.445	1.215
exc.	1.238	1.363	1.
	lengthen	shorten	lengthen

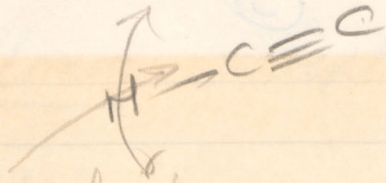


		Ground	Exc.
ν_3	$C{\equiv}C$	2106	1945.8
ν_4	$C{=}O$	1696.9	1304.0
ν_6	$C{-}C$	943.7	951.6
out of plane ν_{10}	$\rightarrow \pi y$	981.2	462.1
imple ν_9		205.3	189.4
ν_{12}		260.6	345.9 $\rightarrow \pi^*$

out of plan

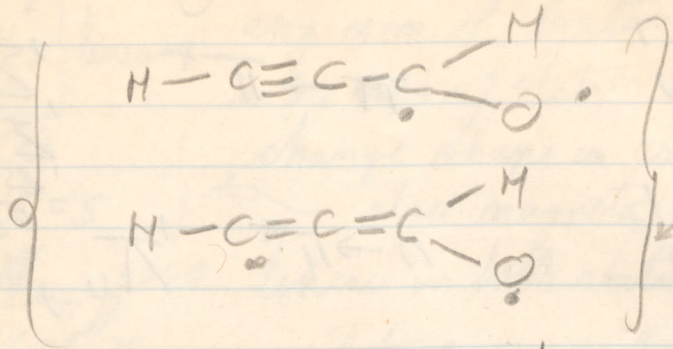
Sept. 24, 1964

(40)

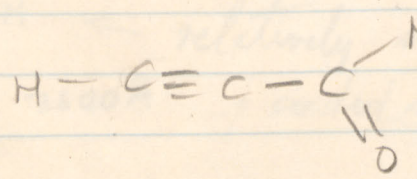


gr exc.

	in plane		
ν_7	a'	650.0	650 unchanged
ν_{11}	a''	692.7	389 different direction



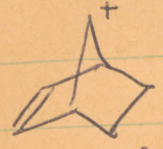
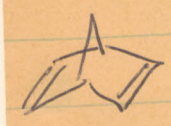
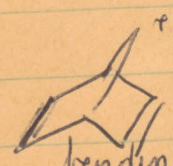
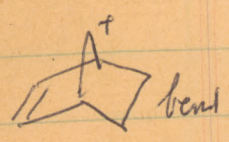
contrib. out of plane easy for H.



≡C–H distance change is also consistent with contributions

1.5 D change in μ.

Radicals in the norbornadiene system

	C^+	$C^\bullet$	
trig	28.509	18.186	10,323
 trig	28,474	18.193	10.281
hole syn	29,482] .170	18,726] .057	10.756
hole anti	29.312]	18,669]	10,643
 trig	28,428	18,192	10,236
 bending	-27	19.422	9.240
	-18.5	18,679	9,824
	-9	18,271	10,203
	0	(18,193)	10,281
	9	18,374	10,053
	18.5	18,894	9,480
	27	19,684	8,667
	36		
	45		
 bent	0	(18,192)	10,236
	9	18,298	10,045
	18.5	18,706	9,468
	27	19,550	8,637
	36		
	45		

i.e very repulsive curves for radicals.

Sept 25

ct. 24, 1964)

(42)

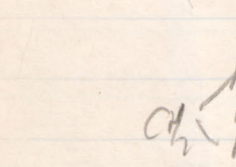
Frey Diazirines Sept. 25

R
R' >C

try a dimethyl diazirine

look at geometry of excited state of $CH_2=N=N$ (2 excited states?)

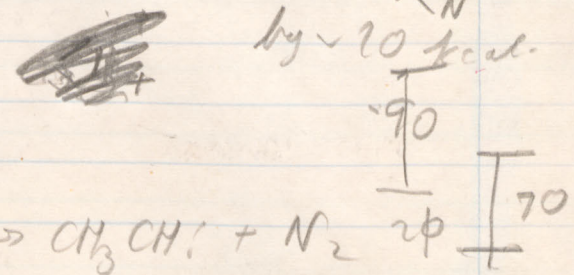
$\epsilon = 100$ 3100 Å



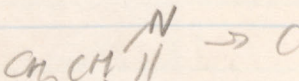
$\longrightarrow CH_2 + N_2$

$\longrightarrow CH_2=N=N^*$

$CH_2=N=N$ as more stable than by ~20 kcal.



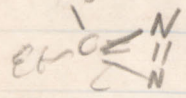
Annich + Bell?
photolysis



$CH_3CH: + N_2$

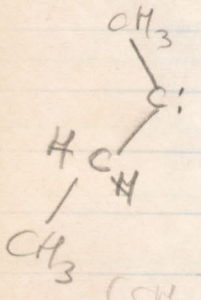
$\rightarrow C_2H_4^* \rightarrow C_2H_4$

$\rightarrow C_2H_2$

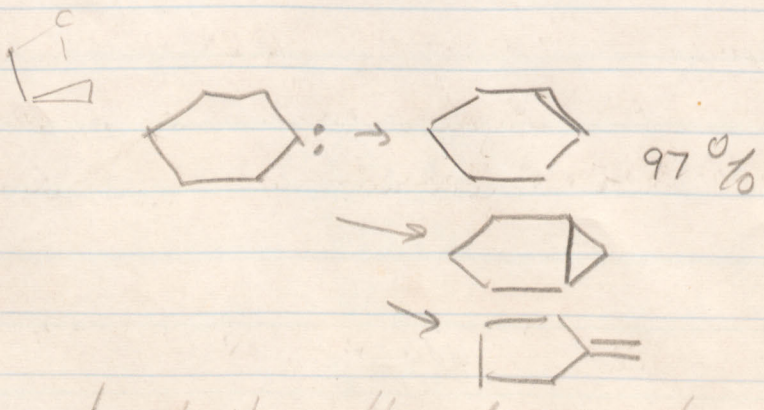


pyrolysis	3.6	66.5	29.5	0.4
photolysis	23.4	38.6	29.5	2.4

close to equil. values.



products different: photolysis → vibr. exc. carbene



Some olefin is formed whose yield is not pressure dependant, i.e. it must be formed not from a ketene, but directly.

(43)

cyclopropene

~~50,10536 f~~		1	
✓47,12268 h		2	✓
55,6073c		3	✓
52,4504c		4	✓
~~51,11066a~~		~~5~~	
IP	53; 17684f	6	✓
mw	53,11997c	7	✓
spect	55, 16157 b	JB	✓
	52, 10666f	9	✓
	58, 11175c	10	✓

↓ (8) KB Wiberg + BJ Nist JACS 83, 1226 (1961)

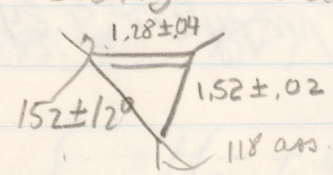
absorption ~~flat~~ fairly flat

185 200 225

much less than for cyclopropene

for C_3H_3· mw JCP 35, 1661 (1961)
JCP 26, 719 (1957)

(2) e.d. JD Dunitz, HG Feldman + V. Schomaker JCP 20, 1708 (1952)
str



(3) M. Simonetta, G. Favini, P. Beltrame
Rend. ist lombardo sci. PtI 91, 311 (1957)
strain energy + geometry of △, ⧋ + ⋈

↓ ~~10~~ (4) Cyclopropene I Wiberg JACS ~~79~~, 4994 (1957)

(7) mwave PH Kasai, RJ Myers, DF Eggers Jr + KB Wiberg
C–C 1.515 H–C–H 114° 42'
C=C 1.300 C=C–H 149° 55'
JCP 30, 512 μ = .455

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Oct. 24, 1964?

Helv Chem. Acta 43, 1766

(44)

59, 15144 g

Ketene, diazomethane bending $=CH_2$

CB Moore + GC Pimentel JCP 40, 1529 (1964)
+ ref see also Cox-Escholt + JCP 38, 1636 (1963)

C=O	0.31
C=C	0.23
C=C=C	0.18
C=C=O	0.086
C=N=N	0.027
(CH_3)	0.064

$k_{bending}$

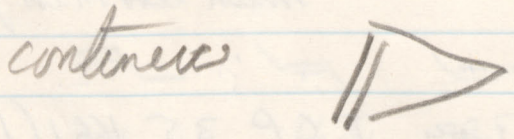
valence structure

$\overset{-}{C}-C\equiv O^{+}$

$\overset{-}{C}-N^{+}\equiv N$

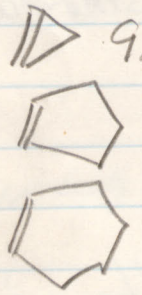
read

---

contenes 

(6) J Collins FP Lossing JACS 81, 2064 (1959)

el. impact I_p



9.95 propylene 9.84

9.27

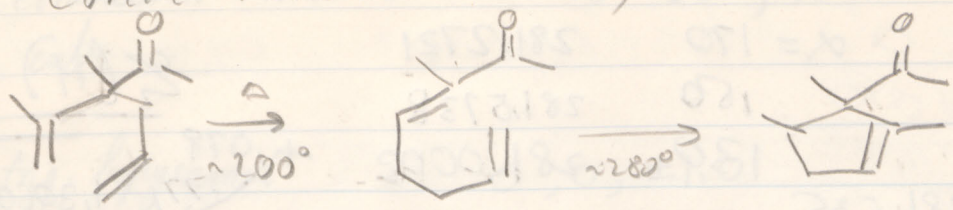
9.18

(10) Strain energy of cyclopropen
KB Wiberg, W.J Bartley + FP Lossing
JACS 84, 3980 (1962)

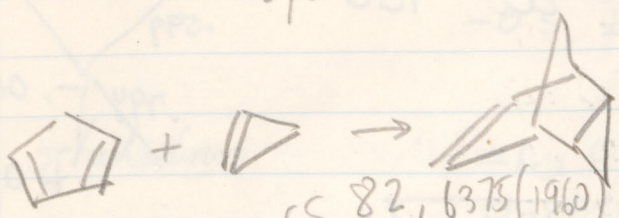
(11) D Peters Tetrah 19, 1539 (1963)
MO theory of (CH) bent bonds
cyclopropen

(12) Review-chemist F L Carter + V. L. Frampton
Chem Rev 64, 497 (1964)

Comia Tetral Let 39, 1964



Cope



JACS 82, 6375 (1960)

IV meeting (sovet) on quantum chemistry
Kiev May, June 1965

A.G. Lerga + M.A. Taylor JCP 41, 1247 (1964)

For uv photolysis of acetone

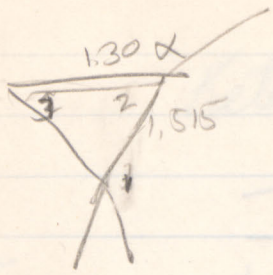
Xe 1470 + 1295 Å Kr 1236 + 1165

higher { → $H_2 + CH_2COCH_3$
→ $H + CH_2COCH_3$

excited states lower { $CH_3 + CH_3CO \rightarrow CH_4 + CO$
$CH_4 + CH_2CO$

(46)

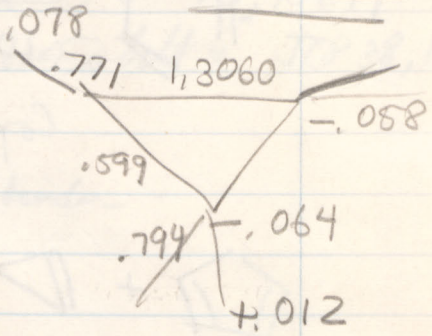
Cyclopropene ma values of Kasa Myers



α = 170	281.2721	
150	281.5738	
130	281.0002	
160	281,535	
155	281,582	
145	281,511	

at 150

$\xi(M) = 1.3$



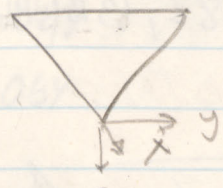
7 −2.947

8 −7.939 π^* a_2

9 −12,702 π b_1

10 −13.143 b_2

11 −13.681 a_1



12.702
7.939
4.763

$b_1 \times a_2 = b_2$ T_y

$b_1 = .2582(H_1 - H_2) - .1740\, C_1 p_2 + .5976(C_2 p_2 + C_3 p_1)$

chang .124 .052 .850

1.70

$\pi \rightarrow \pi^*$ →

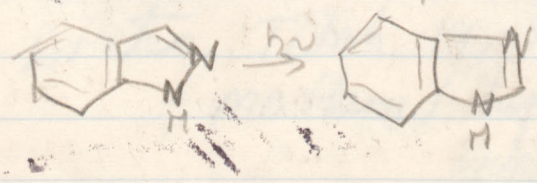
at α = 170 −12.652 b_2

−12.702 b_1 π indep of H

why $b_1 \rightarrow a_2$ so weak compared to □ + ⬠

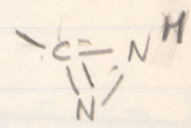
why long wave length tail = $b_2 \rightarrow a_2$? allowed

Tetrah Let. 1964 40 p 2999



tetrahedron X-H 1.0 ±.577350, ±.577350, ±.577350

cube



1-H diazir

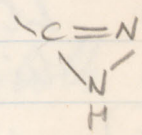
trg. bipyramid 0, 0, ±1.0
1.0, 0, 0
−0.5, ±0.866026, 0 2H

octahedron ±1., 0, 0
0, ±1., 0
0, 0, ±1

icosahedron 0, $\pm \frac{I}{5^{1/4}}$, $\pm \frac{1}{5^{1/4} I\!\!\!\!-}$ permute

diazomethane	diazirine	azirine
~~1 43.8890 d~~	✓7 57.9372 d	C=N·
✓2 49.2183 a ΔH_f	✓8 58.4042 c	CH$_2$
✓3 54.24390 e		2-H azirine
✓4 ✓ 56.9924 i MO		✓9 57.15036 e
✓5 12868 h synth.		✓10 51.14698 b
✓6 58.4530 e		✓11 47.12337 d.
		~~12~~ ~~58~~ 12449 a

1-H diazirine



? 13 57,9828 b

✓ (11) DJ Cram + MJ Hatch JACS 75, 33 (1953)
✓ (2) ΔH_f = 46±6 kcal A. Langer, JA Hipple + DP Stevenson JCP 22, 1836 (1954)
(10) ? S. Yamada et al Yakugaku Zasshi 77, 452 (1957)
→ (3) W. Forville-Thomas + W.J. Jones Z. Elektrochem. 64, 714 (1960)
"First order hyperconjugation in cyanamid ketene + diazomethane

The 16 valence electron system: linear, bent
excited states

OCO $CH_2=C=O$ $CH_2=C=CH_2$

ONO ⊕

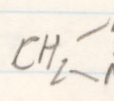
NCN ⊖2

NBN ⊖3

NNN ⊖

FCN $FC\equiv CH$ $CH_3C\equiv CH$ H_2NCN

NCO ⊖ HNCO NCOH HC≡C-OH? cyanamid

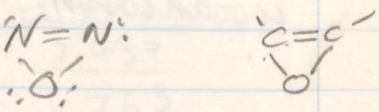
NNO $NN=CH_2$  BH_3CO

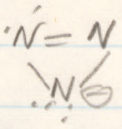
BeF_2 ?

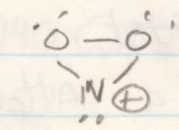
HBO_2?

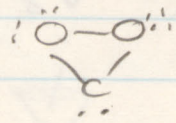
see Lennet's book for arguments:

① why doesn't NNO cyclic exist

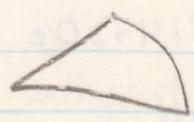


NNN⁻ 

NO_2^+ 

CO_2 

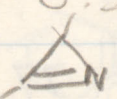
Continue CA



✓ ④ LCAO A.J. Owen, Tetrah 14, 237 (1961) $C=N-N$ (.02, 1.26, 1.24; .87, 1.43)
Hückel ~~sor~~ 3 π orb 2.25, 2.00, 0.59

✓ ⑤ Diazirine synthesis
E. Schmitz + R. Ohme
Tetrah Let 1961, 612

✓ → ⑨ G. Smolensky JOC 27, 3557 (1962)
"azacyclopropenes"
R = Φ, otolyl, n-butyl ←
ε = 112 at 229 mμ; aryl compounds intense abs @ 240.



⑦ structure Pierce + Dobyns

⑧ Mendt

(6) diazirines E. Schmitz Zh. Vseg. Khim Obsch 7,343 (1962)

(11) ~~L. Horner + A. Christmann Ber 96, 399 (1963)~~ + A. Gross

(2) gives mass spectrum at 75°C, 75ev of CH_2N_2

m/e	rel int		
42	0.01	$CH_2N_2^+$	they think this cyclic!
29	0.024	CHN_2H ?	
28	1.0	N_2, CH_2N	$\Delta H_f = 46$
27	0.5	CH_2N	
26	0.44	$C_2H_2^+$? C_2H ? CN?	
25	0.062		
24	0.020		
14	0.020	CH_2^+, N^+ ?	
13	0.007	CH	
12	0.002	C	

cyanamid also cyclic H_2NCN see (3) +
M Davies + W Jones TFS 54, 1454 (1958)

(3) For 1st order hyperconjugation in cyanamide, diazomethane + ketene
Hückel method incl. H (+) (−)
trying to explain high degree of bonding for both CN bonds
+ weakening of X–H bonds
comes out OK, along with bond lengths using Coulson curve

(5) max uv 321 diazirine
diazomethane 412 G Kortum 2 Phys. Chem 50, 361 (1941)
isodiazomethane H C=N-N-H E. Müller + D. Ludsteck
Ber 87, 1887 (1954) 247 mμ in
Körtum: 2 bands in Et_2O I max ~24000 cm^{-1} log ε = 0.8
going up still at 43000 cm^{-1} log ε = 4

(50)

minimum stage ~ .9 for all
w/ electron corr

CH^+	0.5	72.998	12.363	11.40	~1.2 for radical CH_4^{-1} $CH_5^\cdot$
	0.6	73.141	12,594	↓	
	0.7	73,185	12.801		
	0.8	73.140	12.983		~1.4, 1.5 for CH_5^-
	0.9	73.020	13.142		
	1.0	72.841	13.278		
	1.1	72.621	13.395		
CH_4	0.8	142.855	−15.388 f	30.044 f	
	0.9	143.115	−15.502	17.740	.8588
	1.0	142.854	−15.541	9.745	H-H −.0570
	1.1	142.175	−15.519	4.316	
	1.2	141.167	−15.450	0.490	
	1.3	139.910	−15.344	−2.289	
	1.4	138.480	−15.212	−4.358	

CH_5^+ trig bipyr. D_{3h}

				$CH_5^\cdot$
0.8	145.980	−15.641 e	2.217 a	
0.9	146.141	−15.745	−2.448	.0430 a .7616 e
1.0	145.766	−15.771	−5.521	−.0855 a-a .0247 a-e
1.1	144.960	−15.735	−7.685	−.0799 e-e 152.595
1.2	143.812	−15.652	−9.135	152.947
1.3	142.405	−15.531	−10.226	152.631
1.4	140.811	−15.384	−11.033	151.844
1.5	139.099	−15.218	−11.639	150.738
2.0	130.845	−14.353	−13.081	143.926

CH^+	0.9	73.020
CH_4	0.9	143.115
CH_5^+	0.9	146.141
CH_6^{++}	0.9	148.697
CH_8^{++++}	1.0	153.624

Doenna

(51) So energy is no onterion for $CH_6^{(n-4)+}$ it keeps on getting better as d repulsion term is needed. overlap population decreases + bonds begin to form among H's in CH_{20}^{+16}

CH_6^{++} O_h

0.8	148.640	−16.224 f	+1.142 e	−.0880 hus .0188 as
0.9	148.697	−16.295	− 3.216	.6143
1.0	148.213	16.286	6.090	
1.1	147.295	16.216	8.066	155.361
1.2	146.033	16.099	9.468	155.501
1.4	142.781	15.767	11.238	154.019
1.6	139.016	15.361	12.228	151.244
2.0	131.864	14.549	13.132	144.996
3.0	124.790	13.654	13.571	138.361
∞	124.40			

42.80
81.60
124.40

CH_8^{++++}

1.0	153.624	−17.099 f	−4.648 f	.4420
1.1	152.644	17.017	6.888	
1.2	151.292	16.872	8.489	
1.4	147.757	16.484	10.540	
1.7	141.344	15.757	12.116	
2.0	135.068	15.009	12.862	
3.0	125.285	13.733	13.673 q	13.527 f
4.0	124.469	13.617 q	13.608 f	13.593 f

CH_3^+ 1.3 1.1 0.9

120	109.279	11.4	111.288	11.4	112.402	11.4
119	109.217	11.446	111.216	11.438	112.320	11.430
118	109.153	11.491	111.141	11.475	112.236	11.460
116	109.020	11.580	110.987	11.549	112.062	11.520
114	108.880	11.667	110.825	11.622	111.879	11.580

6.7

C_{20}^{+16} .1256

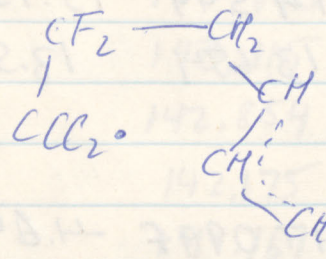
CH_{12}^{+8}	0.6	159.529	−17.832 f / +29.535 h	169.530	19.444	9.604 h
.2823	0.9	162.080	−18.354 f / +0.3906 h	172.273	19.973	−7.983
	1.2	159.222	−18.064 / − 7.571	170.311		
	2.0	141.041		154.506		

(52)

Bartlett ; Cycloadditions: Oct. 6

biradical mechanism ; normally → 4 membered rings

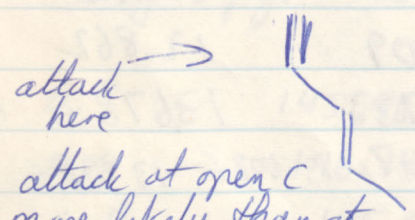
radical terminated by CCl_2 more stable
terminal radical in diene better



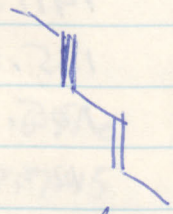
Roberts review in Org. syntheses?

rates are increased by all substitutions at 2 that would favor radical there:

1-2 addition better than 3-4



attack at open C more likely than at substituted C.



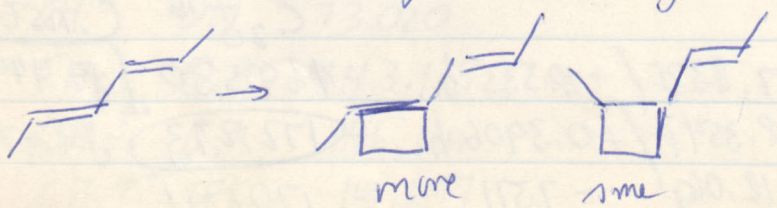
trans-trans
cis-cis
trans-cis

biradical theory
double bond away from ring retain config
but C=C on addition isomerizes.

Montgomery.

not complete equilibration
but somewhat greater
retention of original conform.

barrier should be down.

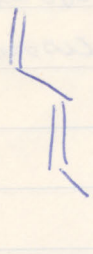


coplanarity → does not
guarantee 1,4 addition
but ~~makes~~

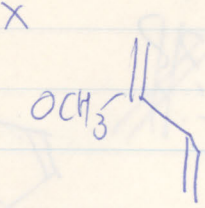
(53)

+ $Cl_2C{=}CF_2$ → both 1,2 and 1,4 products

preferred



gives 3,4 only



gives 1,2.

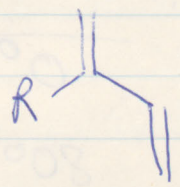
rates not corrected

1,2	17	93
1,4	83	6

photosensitized addition of chloroethylenes to dienes

ketenes add only 1,2 to

1,2 + 1,5 addition comp

1,2; 3,4; 1,4 

$R = CH_3$ no 1,4

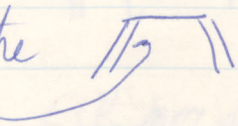
$C(CH_3)_3$ 45% 1,4

Stereochemistry of 1,4 Do product has not been determined.

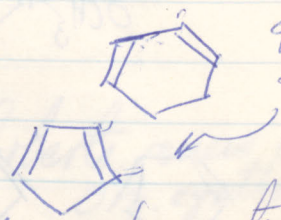
(54)

Diels-Alder requires cisoid

2-t-butyl has strongly hindered transoid → better in cisoid

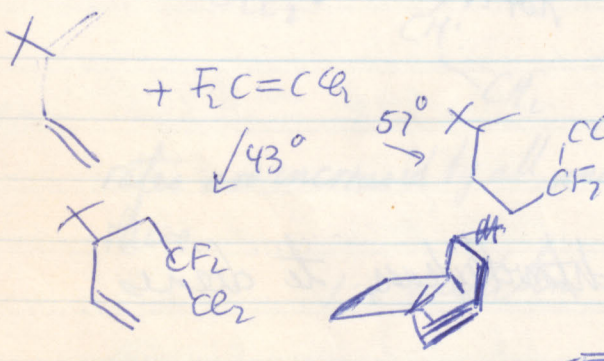
the smaller the angle α  ??

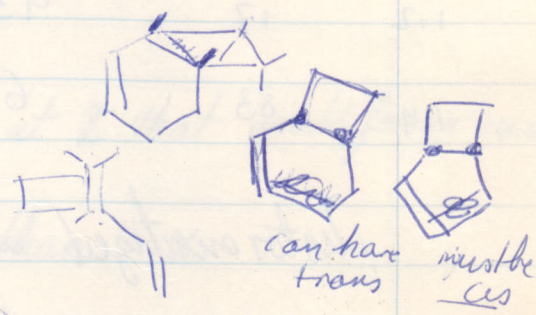
the more 1,4 product.



93;6 1,2
7:83

shown in transoidum state



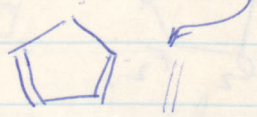


can have trans — must be cis

why would this like to be trans for 1,2

photochemical set of products identical.

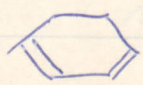
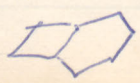
difference only in.

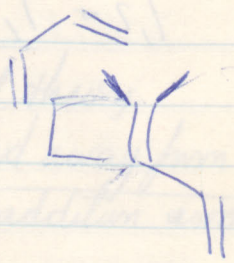


	1,2	1,4	
hν	67	33	0°
Δ	17	83	80°

diff in temp.

excited state is one of these

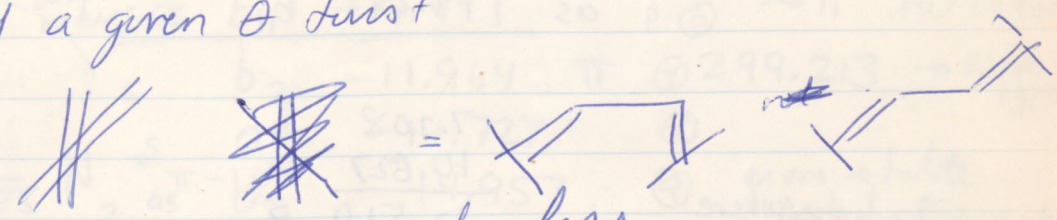
1. hν of  nearly the same as thermal i.e. mainly 1,2.
2. add 



mostly cis

Simple argument for α dep of favored reaction

for little 1,4 interaction, i.e large α what matters is how much is π system uncoupled by a given θ twist



uncouples ~~less~~

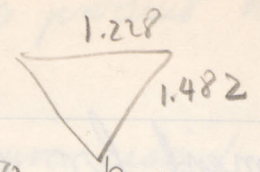
~~that is not what~~ I want

because that is the one favored

~~Why should one look at transform~~

but that's not what one wants for ~~Diels~~ intramolecular reaction

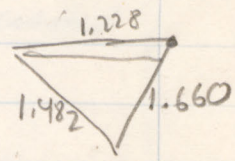
i.e. the larger α, the more is favored the form which wins least the π bonding in the chain



(56)

diazenne

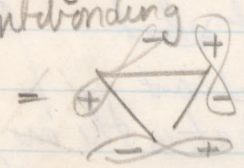
5	s	5.750	b_2	295,963
6	as	10.639	a_2	
7	s	12,766	b_2	π^*
8	s	13.972	a_1	
9	as	14.248	b_1	



7.208	s	
10.627	as	$-\pi^*$
12.510	s	
14.054	s	
14.435	as	π

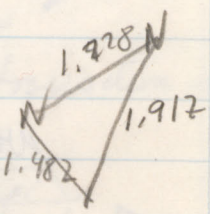
295.971

(5) as everywhere antibonding



∴ 7→5 will also break bonds to N_2

9.520	s	
10.590	as	
11.858	s	
14.252	s	
14.613	as	



295.557

Jammed in $n \rightarrow \pi^*$

			O	dist .2	dist .5
diazenne	ground	s	295,963	295.971	295,557
	7-6	as	293.836	294.088	294.284
	8-6	s	292.630	292.544	291.932
	9-6	as	292.354	292.163	291.534
	7-5	s	288.947	290.669	293.219
	10-6		$a_1 \rightarrow a_2 = a_{2\pi_2}$		
	11-6		$b_1 \rightarrow a_2 = b_{2\pi_2}$		

funny: 7-6 = as correlates all the way.

but in diazenne it wants to open up, in diazomethane it wants to be linear

(5) 7-5 is second lowest in diazomethane + wants to bend; it is not 2nd lowest in vertical diazenne, but also wants to bend.

Frey's picture

diazenne → diazenne *

as

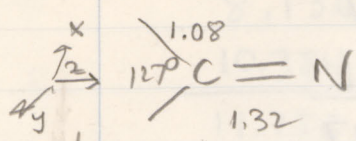
s

(57)

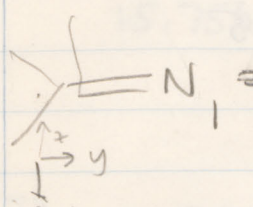
diazomethane

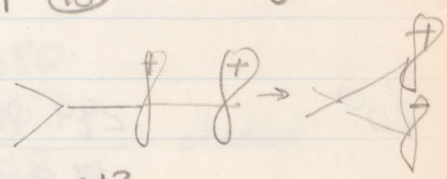
distortion → CH_2 (N, N)

also a curious change of config at CH_2



yz s	b_2	−7.895	π*	⑤
axes as above as	b_1	−9.491		⑥ → π* but ch sym
s	b_2	−11.964	π	⑦ 299.213 → Walsh type
s	a_1	−14.727		⑧
as	b_1	−14.957		⑨ more stable but by too much
s	b_2	15.724	π	⑩





π is N_1–N_2 antibonding
C–N_1 bonding

π* N_1–N_2 antibonding.

299.213
295.963
3.250 = 75 kcal
obs = 30

∴ π → π* (π → σ*) will break C–N_1 → CH_2 + N_2.

now which levels correlate with which in ◁ is problem

				10° in plane	10° out of		
ground	s	299.213	A_1	299.177		299.161	
⑦→⑥	as	296.740	(A_2)	296.744		296.705	
⑦→⑤	s	295.144	A_1	295.117	20°	295.171	
⑧→⑥	as	293.977	(B_1)	294.028	294.128	293.932	293.808
⑨→⑥	s	293.747	A_1	293.703		293.696	
⑩→⑥	as	292.980	A_2	292.979		292.927	
⑧→⑤	s	292.381	(B_2)	292.401	292.413	292.398	292.390
⑨→⑤			A_2				

			10	20	40	60	90
as ⑦→⑥	in	296.740	296.744	296.748	296.652	296.100	293.011
	out		296.705	296.603	296.121	295.021	293.914
s ⑦→⑤	in	295.144	295.117	295.033	294.651	293.852	291.740
	out		295.171	295.245	295.396	295.168	292.255

cross

	in plane	$CH_2=N=N$ bend		out of plane.
10°	299,177			299.161
	7,900		5	7.957
	9.527		6	9,491
	11.960	b_2	7	11947
	14,676	a_1	8	14.720
	15,001		9	14.956
	15.725		10	15,725
20°	299.066			298,999
	7,915			8,137
	9.630			9.495
	11,948			11. 891
	14.569			14.696
	15.083			14.950
	15.727			15,728
40°	298.555			298.232
$C-N_2$ = 2.29	7,984			8.784 s
	9.985			9.509 a
	11,888			11,620
	14,296			14,606
	15.237			14.925
	15.736			15,741

Still conclude that in first excited state the molecule remains approximately linear; in second

Doenng

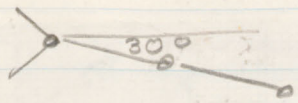
(59)

	in plane	out of plane	
60° C-N. 2,12	297.468	296.445	
	8,136	9.541 a	> checked
	10.384	9,688 s	> checked
	11.752	10.965 s	
	13.969	14.460 s	
	15,302	14.868 a	
	15,756	15,759 s	

90° C-N 1.73	294,234	295.680	
	8,678	7,989 s	> checked
	9.949	9,648 a	> checked
	11,172	11,414 s	
	13,682	14.089 s	
	14.898	14.625 a	
	15.842	15,722 s	

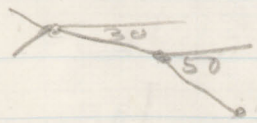
bond beyond to form

tetrahedral distortion.



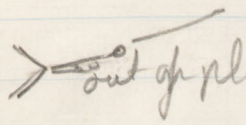
−7,895
−9,112
−11.964
−14.220

298.235
295.383
294.166
} bad



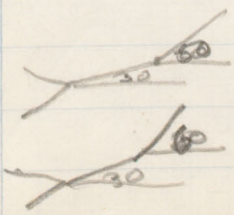
7,915
9,192
11.947

298,212 }



7,989
9,452
12,011

299.087 296528 295.065



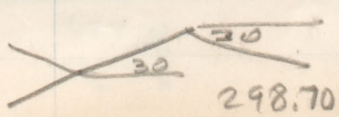
8,280
9,461
11,886

298.793 296.368 295.187

8,582
9,469
11,760

298,461 296.170 295.283

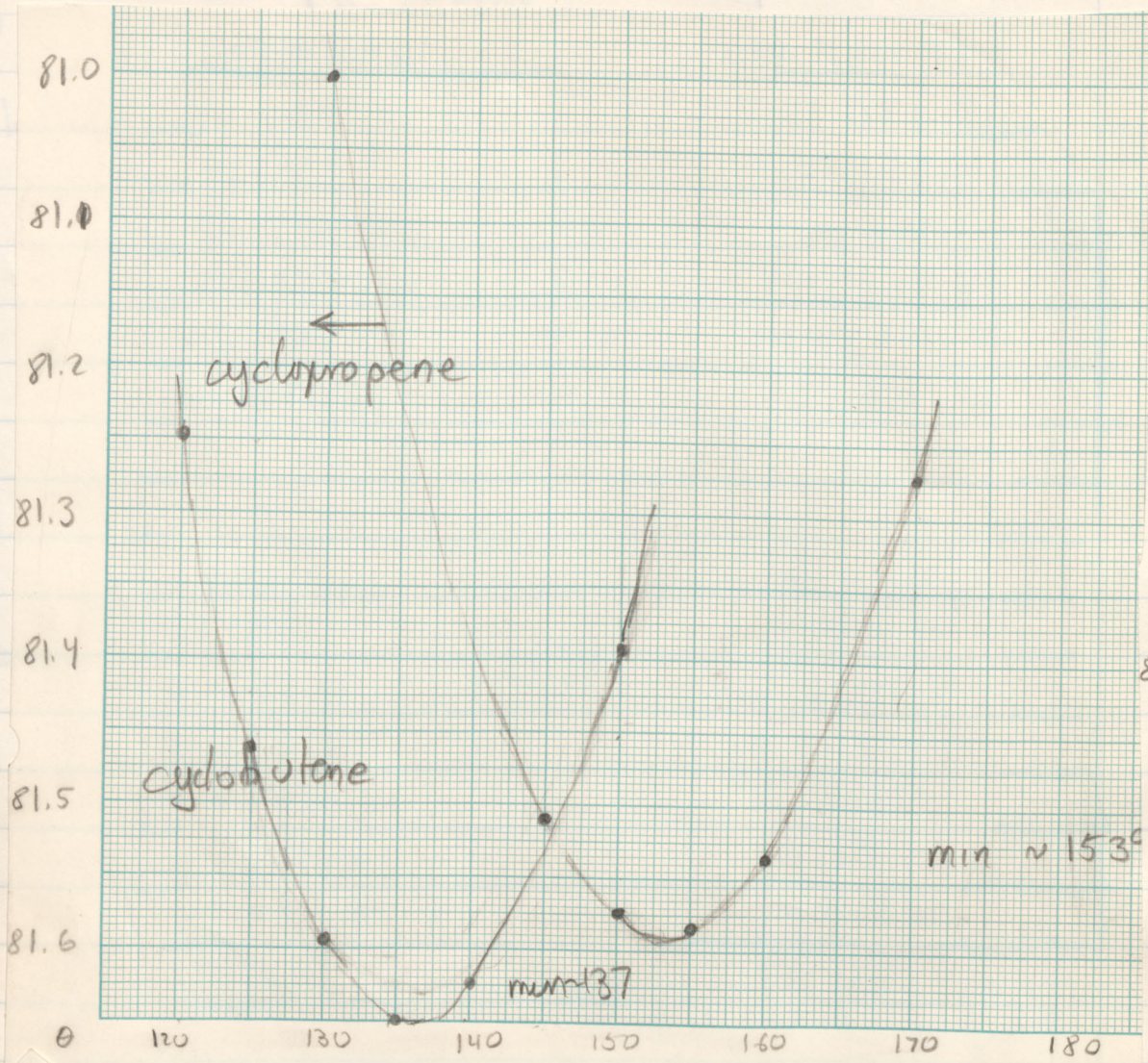
296.252 295.217



8,424
9,459
11,909

298.702

cyclopropene, vary HCC



	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
A_1	1	1	1	1	T_z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	T_x
B_2	1	-1	-1	1	T_y

Deanna

(61)

288
289
290
291
292
293
294
295
296
297
298
299
300

A_1 s
B_2
A_2
B_2 as
A_2 s
B_1 as
3.4ev
2.2
A_1 s
A'
A''
A'
s
as
s
as
s A_1
as A_2
2.5ev
4.1
s A_1

C_{2V} CH_2 N N

C_9

$CH_2=N=N$

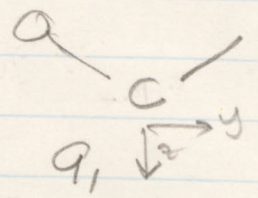
10 X 10 TO THE CM. 358-14B KEUFFEL & ESSER CO. MADE IN U.S.A.

(62)

π butadiene

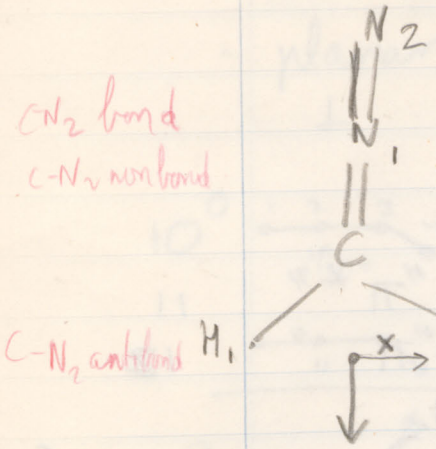
G.A. Kogan + E.M. Popov. HAN 1964, 1393

say 1. Svendsen + Tarasov force field is loose



	CO_2 1.16	a_2	b_2	a_1	b_1
180	324.976	14.739c	7.647c		
170	324.961	14.737,	14.727,	7.765	7.648
160	324.911	14.732,	14.688,	8.094,	7.653
		π+	σ−	σ+	π−
150	324.812	14.721,	14.620,	8.566,	7.661 ± C_2
140	324.635	14.704	14.514,	9.111,	7.675
130	324.334	14.678	14.355,	9.676,	7.696
120	323.826	14.635,	14.115,	10.228,	7.729
110	322.972	14.568,	13.748,	10.754,	7.780
100	321.520	14.461,	13.160,	11.256,	7.859

	5→4 ✓	6→4 forbid	5→3 forbid	6→3 ✓
180	←	317.884		→
170	317.999	317.989	317.882	317.872
160	318.317	318.273	317.876	317.832
150	318.758	318.657	317.853	317.752
140	319.232	319.042	317.796	317.606
130	319.655	319.332		
120	319.939	319.419		
110	319.978	319.168		
100	319.616	318.316		



CN_2 bond

$C\text{-}N_2$ nonbond

$C\text{-}N_2$ antibond

$-7.895\ (a_1)\ 0.678\ C_y - 0.828\ N_1y + 0.593\ N_2y$

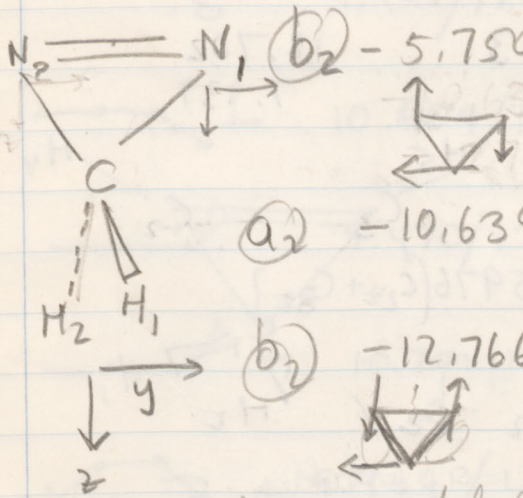
$-9.491\ (b_1)\ 0.186(H_1 - H_2) - 0.013\ C_x + 0.833\ N_1x - 0.791\ N_2x$

$-11.964\ (b_2)\ 0.743\ C_y + 0.251\ N_1y - 0.639\ N_2y$

$b_2 \times b_2 = a_1$

$b_2 \times b_1 = a_2$ forbidden

$b_2 \rightarrow b_1$ CH strengthened



$(b_2)\ -5.750$ $\quad 0.054(N_1s - N_2s) + 0.635(N_1z - N_2z) - 0.852\ C_y + 0.286(N_1y + N_2y)$

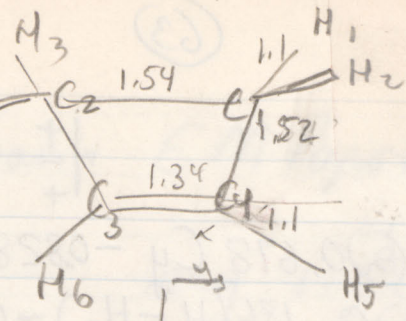
$(a_2)\ -10.639$ $\quad 0.798(N_1x - N_2x)$

$(b_2)\ -12.766$ $\quad 0.113(N_1s - N_2s) - 0.536(N_1z - N_2z) - 0.559\ C_y + 0.186(N_1y + N_2y)$

note π orbitals in diazomethane become σ orbitals in diazirine; σ orbitals in diazomethane become π like orbitals in diazirine.

Lowest energy transition changes from a $\pi \rightarrow \sigma^*$ to a $\sigma \rightarrow \pi^*$ and more important becomes allowed; while $\pi \rightarrow \pi^*$ becomes $\sigma \rightarrow \sigma^*$ and forbidden.

Cyclobutene



170°	385.270
150°	386.928
130°	387.194
110°	386.169

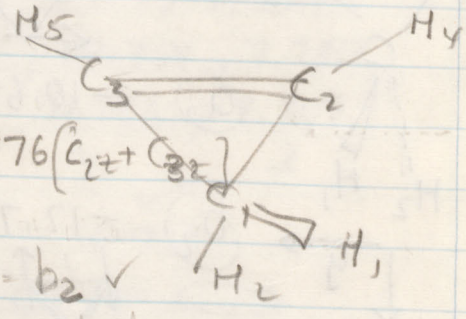
at 130

−7.995 "π*" 11
−12.769 "π " 12
4.774

(11) $-0.1303[H_1 - H_2 - H_3 + H_4] + 0.0084[C_1z - C_2z] + .8173[C_3z - C_4z]$
95% π

(13) $0.1450[H_1 - H_2 + H_3 - H_4] - 0.0992[C_1z + C_2z] + .6145[C_3z + C_4z]$
90% π

cyclopropene (130) 4.763 12.702
nearly same 7.939



(8) $.8381[C_2z - C_3z]$
(9) $-.2582[H_1 - H_2] - .1740\,C_1 + .5976[C_2z + C_3z]$

one center terms only $b_1 \to a_2 \cdot b_2$ ✓
$a_1 \to a_2 = a_2$ forbidden σ

$\mu \propto .5008$ △
$.5022$ C=C □
$.0008$ C_z
$.0150$ H

so it really can't explain difference in △ + □ intensities

These angles 153 are what one would expect for
137 bisecting angles

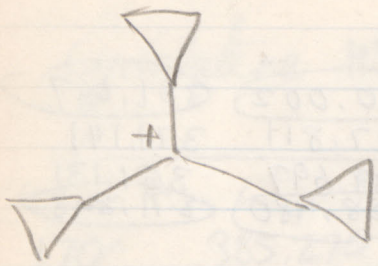
△ $\alpha_3 = \frac{360-60}{2} = 150$
$\alpha_4 = \frac{360-90}{2} = 135$

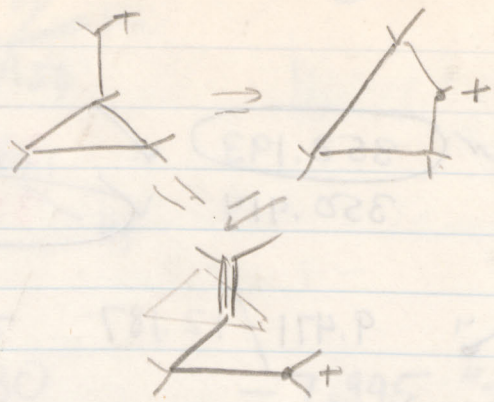
Deanna

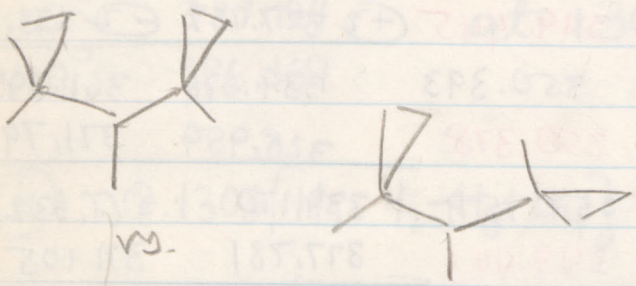
(65) Butatriene, Bending Cchain

planar	352.193 ✓	349.476	340,002	361.667	
			327.811	371.141	
⊥	350.414 ✓	350,414	339.697	361.131	
			328,980	371,848	
10°	9.471 / 12.187	352, 161	(+1) 339.974	(−1) 361.632	
		349.445	(+2) 327.787	(−2) 371,103	
	10,702 / 10.717	350.393	339.676	361.095	
		350,378	328.959	371,797	
	9.473 / 12.189	352.159	339.170	361.632	
		349,443	327.781	371.105	
	10,713 / 10.729	350,404	339.675	361.117	
		350,388	328.946	371.830	
20°	9,464 / 12,176	352.061	339.885	361.525	
		349.349	327,709	370.989	
	10.654 / 10.716	350.329	339.613	360.983	
		350.267	328.897	371.637	
	9.470 / 12.185	352.053	339.868	361.523	
		349,338	327.683	370.993	
	10.701 / 10,767	350.373	339,606	361,074	
		350,307	328.839	371,775	
10°	9.469 / 12.157	352.097	339.940	361,568	
		349.409	327.783	371.035	
	9.469 / 12. 211	352.160	339.949	361.629	
		349.418	327.738	371.098	
	10.697 / 10.713	350.354	339.641	361.051	
		350.338	328.928	371.748	
	10.713 / 10.732	350.386	339,654	361.099	
		350,367	328.922	371.812	

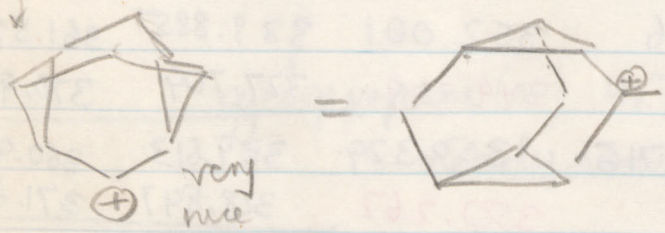
So unlike allene; no bending here
even though one could write good
resonance structures







vs.

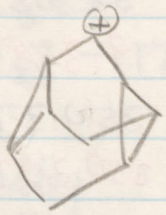


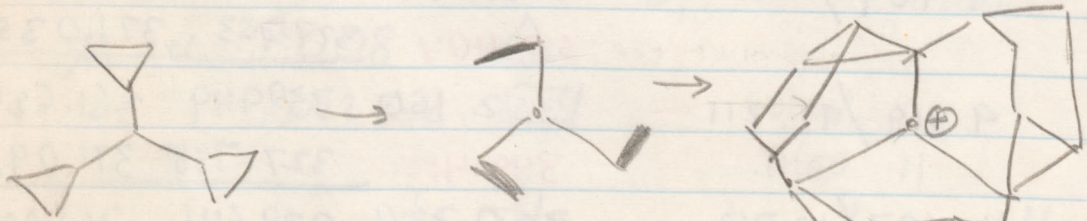
very nice

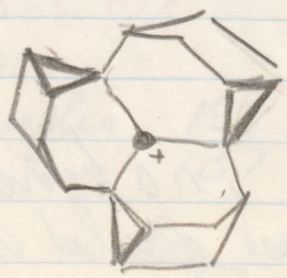
very symmetrical.

possible dications?
trications?

possible H shifts?

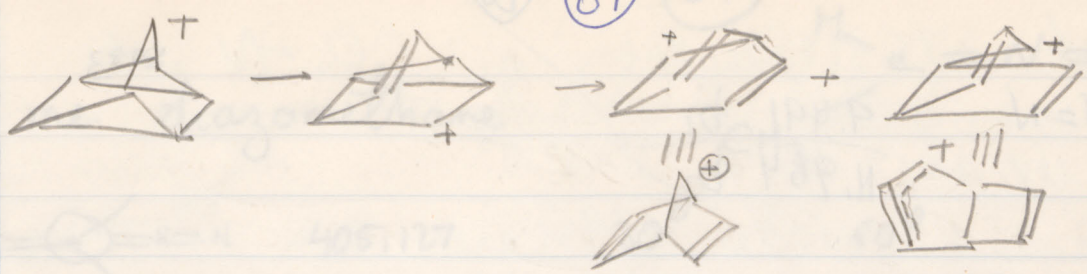






Doenng

(67)



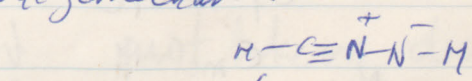
Schmitz review
AC Int ed, No. 5

H's on diazirine? △

Herzberg on CH_2, CH_3 PRSA 262, 291 (1961)
spectr. IP diazomethane 9 eV
mass spect 9.13

Steacie looks 1954 good source on photolysis

Do some calculations on isodiazomethane.

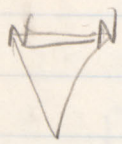


position of M·s

(68)

8083

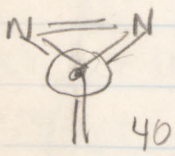
$CH_2=N=N$ 9.491 b_1
11.964 b_2



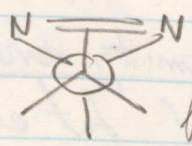
10.639 a_2
12.766 b_2

3.2

methyl diazirine $C^{1.54}-CH_3$



401.925 30° 401,949 60° 401.972 =



barrier = 0.047
= 1.1 kcal.

5.780 5.604
10.639 −10.637
12.766 −12.606
13.972 13.624
14.248 13.969

∴ shift to long wavelength
0.158 ev
= 1280 cm^{-1}

2.127
1969

3.2 cm methyl cyclopropene

obs 1760 (Raw)

symmetry C_s

10.637 $0.018(H_1-H_3) + .006$ $0.798(N_1x-N_2x)$
no change

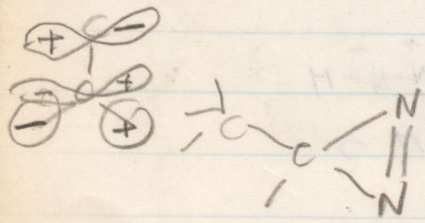
12.606 $.128(H_1-H_3) + .1021(N_1s-N_2s) - .5477(N_1z-N_2z)$

change for 2 in 12.606 $-.5323(Cy) + .098\,C_{me}y + .1724(N_1y+N_2y)$
.03 to each H
.02 to C $-0.0075(N_1x+N_2x)$

new axes

only change now is that 12.606 is slightly C_1-C_{me} antibonding.

$C_{me}-H$ bonding consistent with $\pi \to \pi^*$ leading to rearrangement to ethylene



but this is not worth pushing.

me diazomethane

405,127

30° 60°

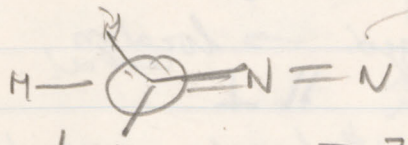
405,132 405,137 0.010

= 0.2 kcal.

orientation gem methyl

allene calc 1.3

+propylene



original H	8	7.764	2,473 hfm
9,991	9	9.424	2.304 ne
11.964	10	11.728	.169

both levels destabilized calc red shift 1370 cm⁻¹

obs.

exp. shift est from Brinton + Volmer

3950 CH_2N_2 25,320

4600 CH_3CHN_2 21,740

3,580 cm

≈ 3500 cm⁻¹

high → low 4069 − 3964 = .105 850 cm⁻¹

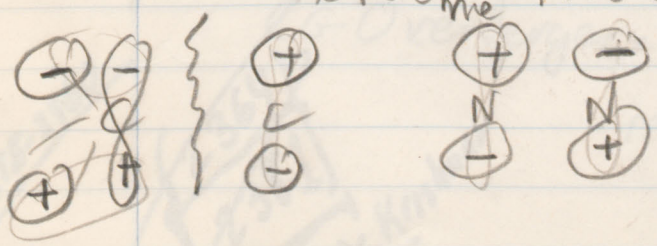
checks also that shortwave length band is redshifted

in diazirine if short λ is redshifted it is $^1B_2 \leftarrow A_1$,

if no shifted $A_1 \leftarrow A_1$

π at 11.728 .743 C_y + .251 N_1y − .639 N_2y

−.093 C_{me} + .706 C_y + .301 N_1y − .648 N_2y.



just like in diazirine

Walsh JCS 1953, 2266 on CO_2 & N_2O

uv abs N_2O 3000 Å°
CO_2 1700

transition $\pi_g \rightarrow \pi_u^*$

bonding → bonding
in equ. atom

less tightly bound in NNO

more tightly bound in NNO

N_2O CO_2

Spoelm; Sponer & Teller RMP 1941, 13, 75

~~47, 11948 g~~

~~52, 9876 a~~
~~48, 5648 f g~~
~~53, 3802 i~~
~~51, 9492 e~~
~~56, 945 f~~

Structure AE Douglas & CK Møller
JCP 22, 275 (1954)

N–N 1.126
N–O 1.186

cc Costain JCP 29, 864 (1958)

Class. structure for N_2O
DVL Griffiths & WJ Orville-Thomas
Chem & Ind 1961, 430

Some more on butatriene distortions.

10° —— 10	// //	352.127	9.471 / 12.186	= ⊥	⊥ 339.94 | 361.896
		349.412			327.755 371.069
	// ⊥	350.385	10.714 / 10.737	339.648	361.099
		350.362		328.911	371.813
	⊥ //	350.361	10.692 / 10.712	339.649	361.055
		350.341		328.937	371.745

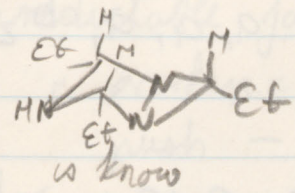
no good, any of them

Diazirdine ; isomeric with hydrazone

$Me_2C{:}N{:}NH_2$

Angew Chem 71, 283 (1953)

E. Schmitz Ang. Chem 76, 197 (1964)
Int. 3, 333

compound 

is know

E. Schmitz · K. Schenkowski
Ber 97, 49 (1964) no NMR

says diazirine more stable ?

E_a diazirine = 33.165 kcal/mole quoting Frey JCS 1962, 3865

1963 1405

C G Overberger + J P Anselme Jetrah Let 1963, 1405

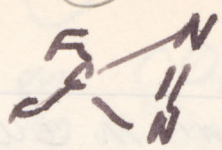
rearrangement at what T? → C=N=N cyclic alkene

607 275-3460

2364
2381

Dr. Krishnan
4235

607 AR5 - 1
275

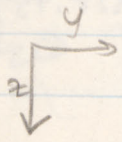
Pimentel: CF_2 from 

A. J. Merer Can J Phys 42, 1242 (1964)

CH_2N_2 below 2000 Å

1900 Å band → 3 transitions within 200 cm⁻¹

$^1B_1$ $^1B_2$ $^1B_1$ in order assigned



switch x↔y from mine

has $a_1 b_2 a_1 a_1 b_2 b_1 b_2 b_1 \mid b_1 b_2$

says near UV + visible = $^1A_2 \leftarrow {}^1A_1$

I have $a_1 a_1 a_1 b_1 b_2 b_1 a_1 b_2 \mid b_1 b_2$

switch to his not

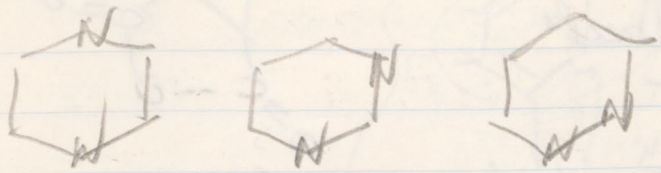
$a_1 a_1 a_1 b_2 b_1 b_2 a_1 b_1 \mid b_2 b_1$

1 2 3 4 5 6 7 8 | 9 10

7 → 9, 10 gives B_1, B_2

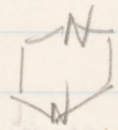
Innes

doesn't see other $n \to \pi^*$ state



	a_g 11.96	b_1 12.36	b_1 12.25
	b_{1u} 13.85	a_1 13.15	a_1 13.04
S lone pair	.0047	.0067	.0714

level ordering correct i.e $n \to \pi^*$ is $b_{2u} \leftarrow a_g$ = $^1B_{2u}$ (3)

i.e for  it is symmetric combin. higher for other 2 antisym.

behavior predictable for 1,3 1,2
overlap = + ∴ splitting would push − overlap one up.

not in line for 1,4
Split > for 1,4 because levels are fairly unique in symmetry D_{2h}, but not for C_{2v}

11.96 a_g	12.36 b_1	b_1 12.25
13.85 b_{1u}	13.15 a_1	a_1 13.04
16.22 a_g	14.43 b_1	a_1 14.37
	14.68 a_1	b_1 14.48
	15.38 b_1	a_1 15.43
	15.77 a_1	a_1 16.3)

Oct 19?

74

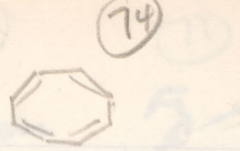
Huisgen, Oct. 19 / Arnett

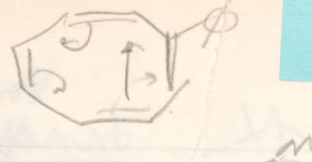
single diequil takes place much faster

Diels-Alder adduct

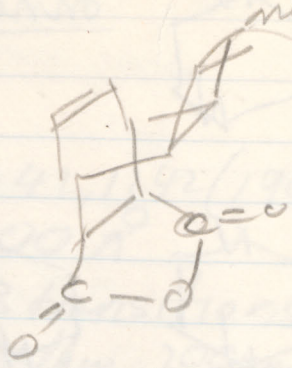
nonplanar COT.

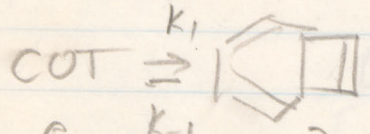
∞ not in geometry to react





only ϕ are isomers does ϕ outs +





ϕ COT gives only ϕ on

$$COT \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \quad 13 \quad \xrightarrow{k_2} \underset{D}{\text{Dienophile}} \quad \underset{A}{\text{adduct}}$$

$$\frac{dA}{dt} = k_d C \qquad k_d = \frac{k_1 k_2 D}{k_{-1}}$$

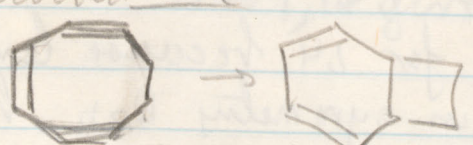
ΔH for rel system	27.4	$\Delta S^{\ddagger}$ −1 e.u
ϕ COT	24.1	$\Delta S^{\ddagger}$ −5

K = 0.0001 approx at 100°

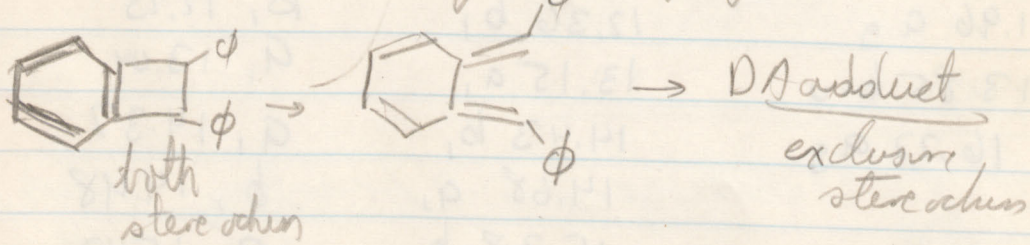
ΔF ≈ 7.3 kcal

large −ΔS implies high order in transition state

for cyclooctatrene



→ favored only by 1.5 kcal

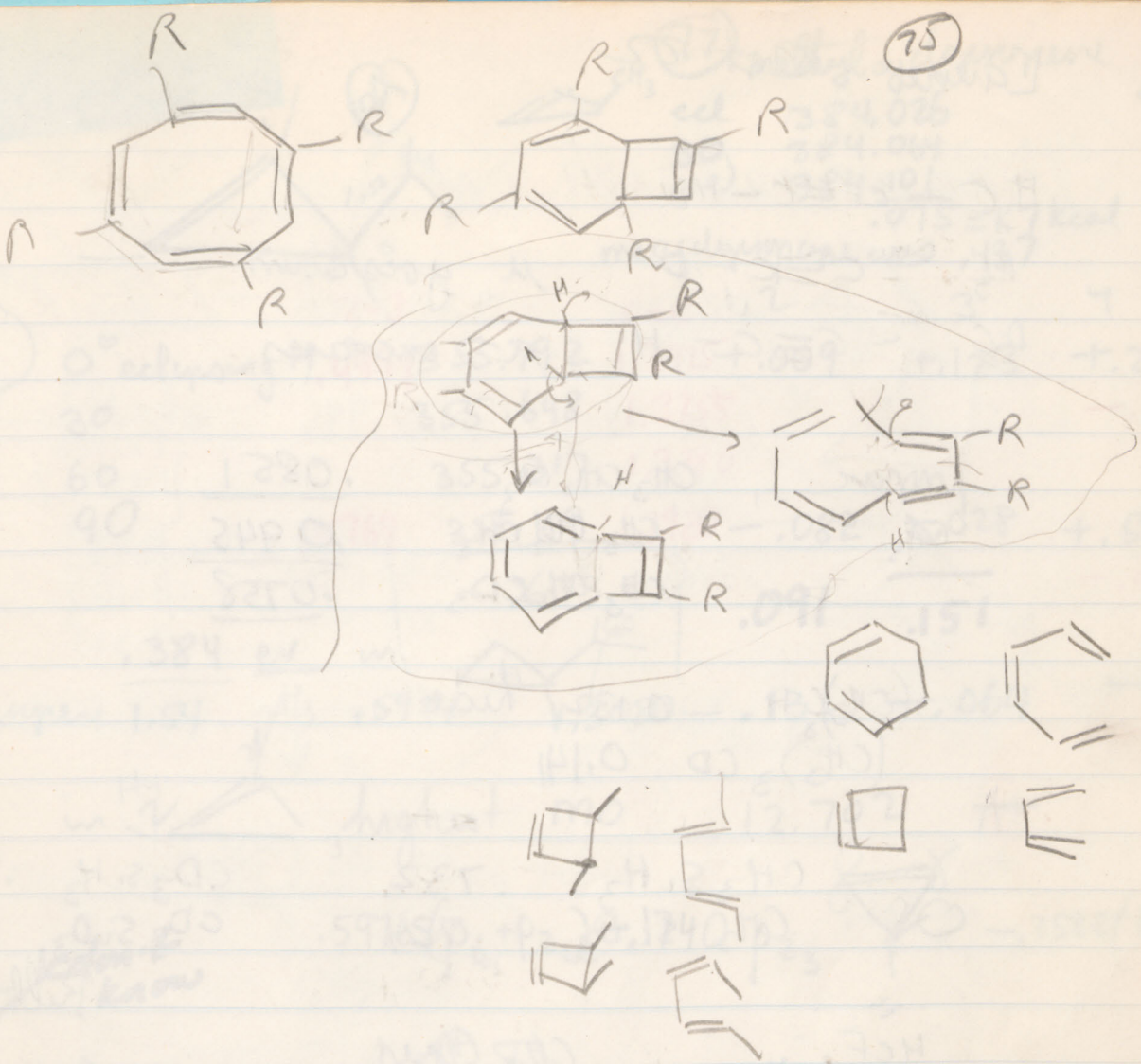


both stereochem

→ DA adduct

exclusive stereochem

Hahn addition to COT takes place at low temp, so it doesn't go through bicyclic compound


R
R
R
R
R
R
R
R
H
R
R
H
R
R
R
R
H

Oct 22

Lavrie Oct 22 (76)

$H_3C-C\equiv C-H$

$H_2C-C\equiv C-D$ μ goes down

$D_2C-C\equiv C-H$ μ increases

CH_3CD_3 →

propane CH_4	$CH_3CH_2CH_3$	.0851
	$CH_3CD_2CH_3$	.0945
	$CD_3CH_2CD_3$	.0758

CH_3D D

$(CH_3)_3CH$ 0.132 Lide

$(CH_3)_3CD$ 0.141

CH_3SiH_3	.732	CD_3SiH_3	.755
CH_3SiD_3	.724	CD_3SiD_3	.750

Kilb

HCF_3
DCF_3

CH_3 CD_3

NMR shifts: H more electronegative than D; acidities

H bigger ⇒ C–H longer than C–D

the shorter, the more polar

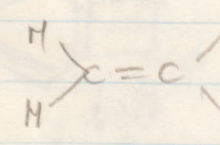
bond distance change

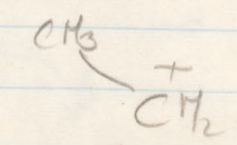
C–D more polar

C^-D^+

C–H

←





anomalous

μ CH_3F 1.9

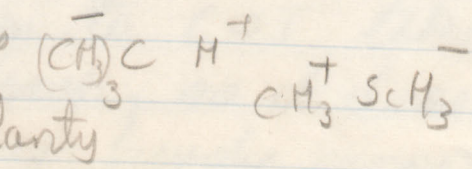
SiH_3F 1.3

GeH_3F 2.4

assume ethers

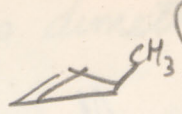
deuterium dipole goes up

⇒ $CH_3C\equiv C^-H$ polarity



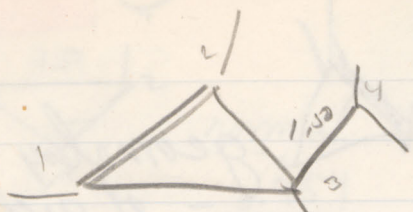
cyclopropyl → allyl

(77) methylcyclopropene 1.54 c–c



ecl 384.026
30 384.064
60 384.101
.075 = 1.7 kcal

methylcyclopropene was .137



2–3

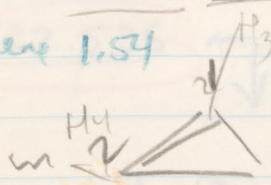
		c=c	1,2	3	4	2–4
ζ_H = 1.0	0° eclipsing H, .4994	355.792	1.3925	+.009	+.123	+.241
	30	355.648	1.3755			−.0506
	60	355.317	1.3280			
	90	353.119	1.2920	−.082	−.028	+.554
		.5769				−.0576

.091 .151

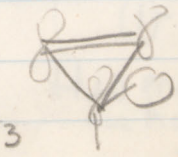
.673

.384 ev

methylcyclopropene 1.54 .5994 .3080 −.131 −.064 −.392

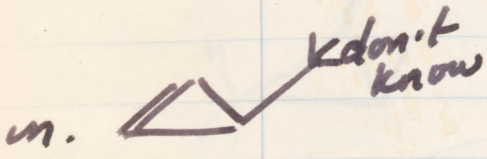


highest MO 12.702 π

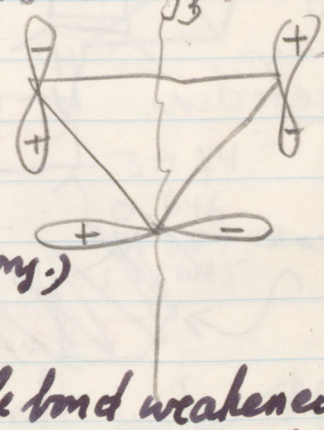


$.5976(p_{z_1}+p_{z_2}) - .1740\, p_{z_3} - .2582(H_1-H_2)$

next σ



$\zeta_1 = 1.3$ $.2072(H_3-H_4) - .0681(S_1-S_2) - .3667(X_1-X_2)$
$+.6828\, y_3 + .0018(y_1+y_2)$



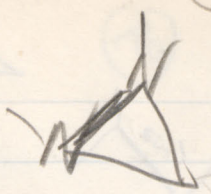
in. I don't know

but in

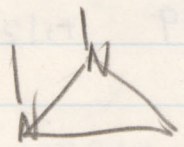
in 0° $H_{1,2}$ more +
90° H_3 more + ("better hyperconj.")

Thus 1. single bond weakened in favor. orient. (in accord with form of
2. double bond strengthened
?

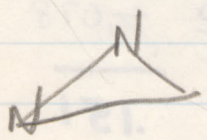
R. Breslow, J. Lockhart & A. Small
JACS 84, 2793 (1962)
concl: transition state close to starting con
no interaction with double bond

Diazindine with  geometry of cyclopropane

planar 330.190
(1.087)


cis H 330.996
(1.10)

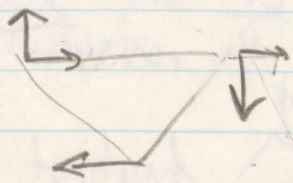
6.373 a"
12.126 a"
14.147


trans H 330.830

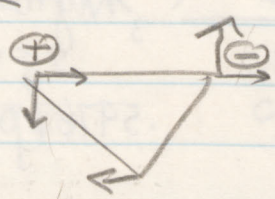
6.373
12.107
13.325

C_s

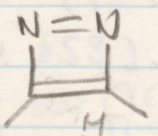
7 a"

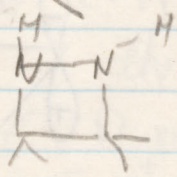


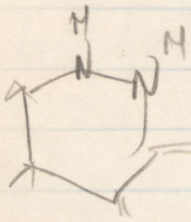
8

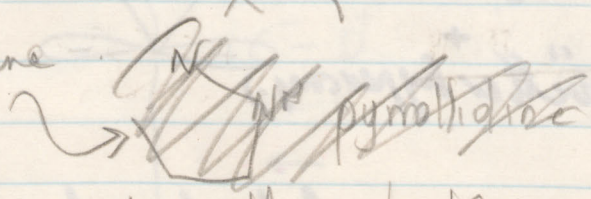


checked to 57

1,2 diazete  → C=C–N=N

1,2 diazetidine 


pyrazolidine


pyrrolidine a lot

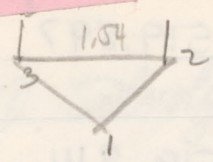
53 19556e died through 1959
Pfizer + Donald JACS 81, 3213 (1959)

cyclopropyl → allyl

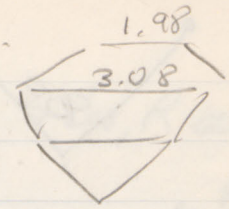
~~Diels-Alder~~

Doering

(PA) cis,trans dimethyl cyclopropyl cations for deRey

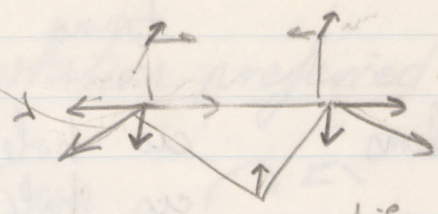


normal △, CH_3 eclipse H



cis −3.954 −12.447 −12.645

522.372

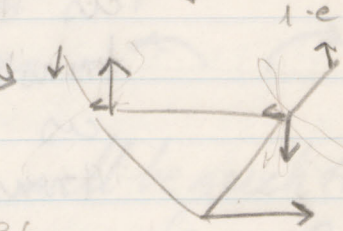


2-3 bonding

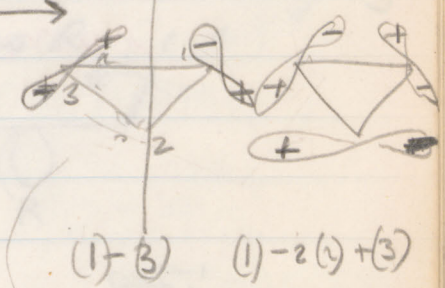
trans −3.967 −12.415 −12.698

522.536

i.e



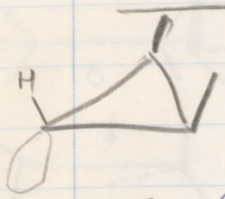
△ = 536 372 .162 ev = 3.7 kcal



(1)−(3) (1)−2(2)+(3)

this one is higher

cis cation, hole trans tebah

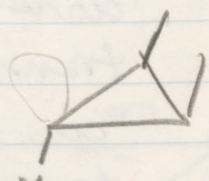


−3.954 −10.987 −12.645 −12.668

29.926

492.446

cis cation, hole cis



−3.954 −11.155 −12.541 −12.645

492.142

30.130

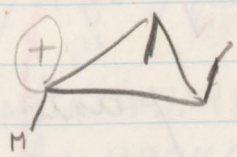
cis cation, trng

−3.954 10.646 12.589 12.645

493.047

29,325

trans cation tebah



3.967 11.088 12.561

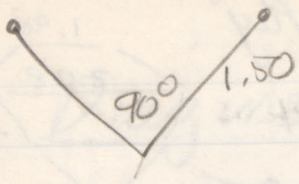
492.480

30,056

trans, trng. 493.224.

29,312

∴ order of reactivity cis, hole anti > trans > cis, hole syn



(80)

as −8.847 −11.432 −12.717 519.897

trans 519.914

catums	cis hole as	491.094	28.803
	cis hole trans	491.749	28.149
	trans hole as	491.443	28.471
	cis trig	492.026	27.872
	trans trig	491,988	27.926

same order as before
note cis catiom trig > trans
reverse for hydrocarbon

10.° motion

1.720

hole trig ✓syn cis 491.916 10.183
✓syn trans 491.857 10.285
++ = out ✓anti cis out ++ (492.146) fav. 9,983
−− = in ✓ " cis in − 491.902 10.122
✓ " trans (492.020) fav. 10.087

hole cis ✓syn cis 491.010 10.454
" trans 491.341 10.318
✓anti cis out 490.661 10.608
✓ " cis in − (491.413) fav. 10.188
✓ " trans 491.034 10.444
hole trans ✓syn cis 491.670 10.091
✓ " trans 491.341 10.318
✓anti cis "out" (492.011) fav 9.843
✓ " cis "in" 491.333 10.260
✓ " trans (491.756) fav 10.019

same

syn

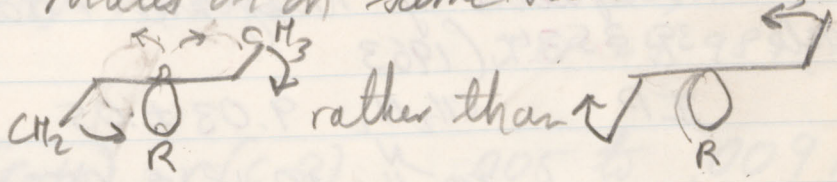
: the less favored direction (in or out) is sometimes worse than other mode

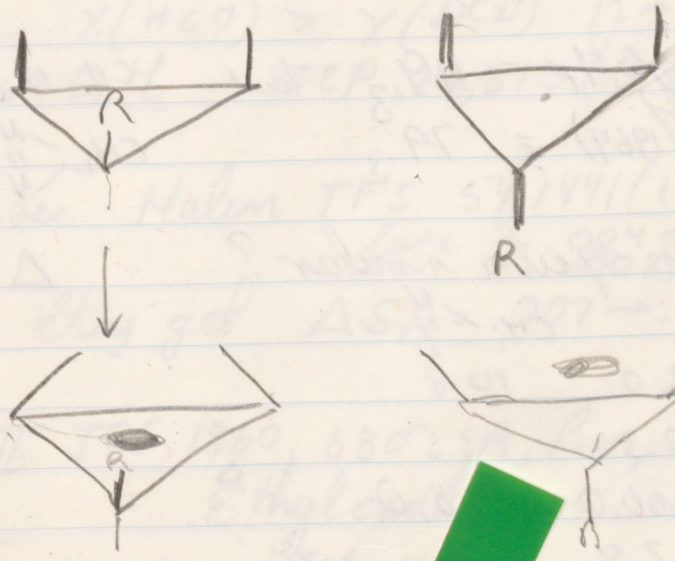
(1) Solvolysis order cis, R trans > trans > cis, R cis

(2) ↻↺ mode of rotation preferred to ↻↑ R

but cis, R, cis ↶↷
cis, R trans ↷↶

(3) for trans, rotation will be such that one CH_3 rotates in on same side as R, i.e.

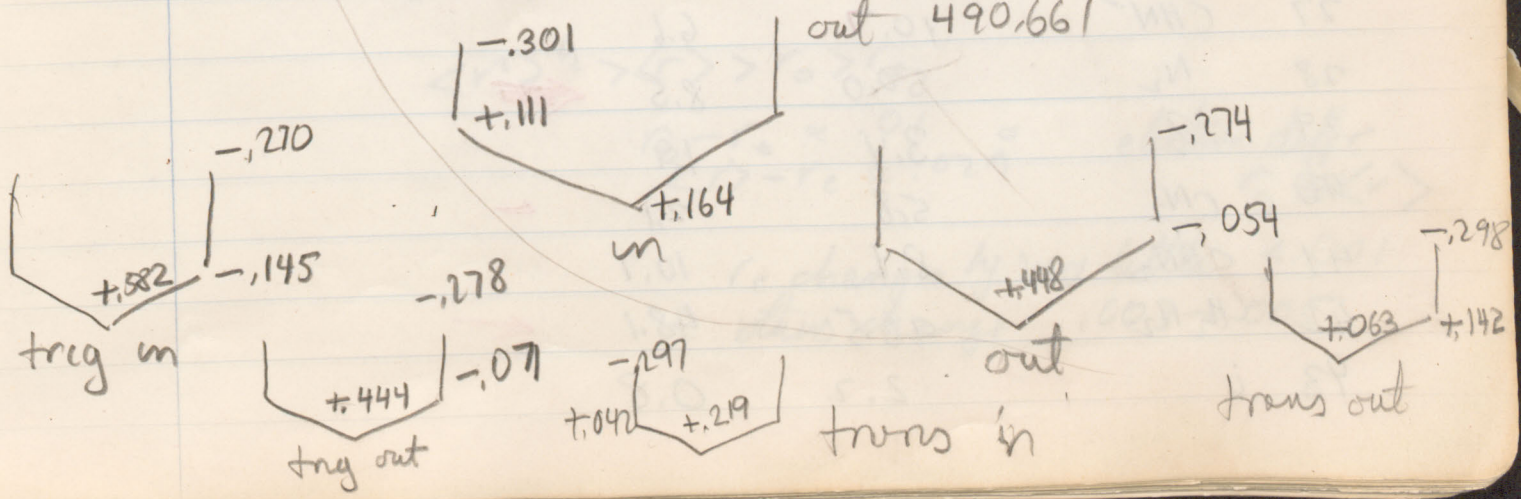




first member of cis

effect = stabilizing of e.d. on backside of leaving group

hole as, des motion in 491.413
out 490.661



cis-trans conform in peptides, amides

LA La Planche + MT Rogers
JACS 86, 337 (1964

JCP 39, 825 (1963) GS Paulett + R. Ettinger
Mass Spectra of Diazirine + diazomethane
errata 39, 3534 (1963

IP CH_2N_2 9.03 ± .05 Hegberg 9.00
$CH_2{<}^{N}_{N}$ 10.18 ± .05 Mercer 8.99

See also
J.A. Bell JCP 41, 2556 (1964) ΔH_f = 49.3 kcal CH_2N_2
GSP + RE JCP 41, 2537 (1964) = 79.3 $CH_2{<}^{N}_{N}$

$\Delta\Delta H$ = 30 kcal

Mass spectra similar?

		CH_2N_2	$CH_2{<}^{N}_{N}$
12	C^+	13.0	10.8
13	CH^+	32.3	23.5
14	CH_2^+	100.0	100.0
15	i	2.9	1.9
20	CN_2^{++}	0.1	—
20.5	CHN_2^{++}	0.6	—
21	$CH_2N_2^{++}$	2.8	—
26	CN	4.7	2.3
27	CHN	10.7	6.6
28	N_2	50.0	8.5
29	?	3.4	1.9
40	CN_2	5.8	2.1
41	CHN_2	8.4	10.7
42	CH_2N_2	96.5	48.1
43	i	2.2	0.8

R. Pauncz + E. Halen JCS 1959, 1967
Effect of Deuteration on Electron Distribution and Energy of Conjugated Molecules.
I. LCAO-MO treatment of toluene.

II EA Halen + R. Pauncz p. 1974
II. LCAO-MO treatment of [α-$^2H_3$] toluene

r(C-H) r(C-D) JCP 20, 1112 (1952)
JCP 24, 989 (1956)

r(C-H) > r(C-D) .005 to .009 Å°
X(HCH) > X(DCD) 12 → 15°
for C_2H_6 JCP 20, 313 (1952) Δr = .0027
ΔX = 17.4°.

see Halen TFS 54, 1441 (1958)
have .004 → .009 Å°
.0035 → .005 and
they get $\Delta S_{12} \approx .007 \rightarrow .004$ for $S_{12} \approx .625$.

III JCS 1960, 630 A. Ron, EA Halen + R. Pauncz.
Ethyl carbonium ion + its methyl deuterated analogue
D.R. Herschbach + VW Laurie JCP 37, 1668 (1962)
V.W. Laurie + DRH JCP 37, 1687 (1962)

r_0 ← zero point nbr. r_e $\langle r^2 \rangle^{1/2}$ $\langle r \rangle$

$\langle r^2 \rangle^{1/2} > \langle r \rangle > r_0 > r_e$

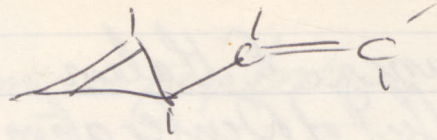
$r_0 - r_e \approx .01$ Å°
$\langle r \rangle - r_e \approx .02$ Å° electron diffr $r_g \cong \langle r \rangle$

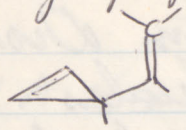
r_e changes by very little < .001
others change .003 → .005

~~Ver. 3~~

(89)

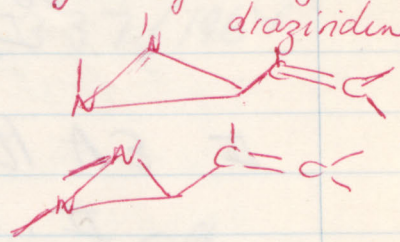
Vinyl cyclopropene rot



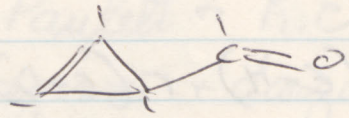


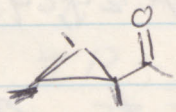
endo	455.133	.122
60	455.064	.191
90	455.041	.214
120	455.094	.161
exo	455.255	0

try ring diazirine.
diaziridine



cyclopropene carboxaldehyde

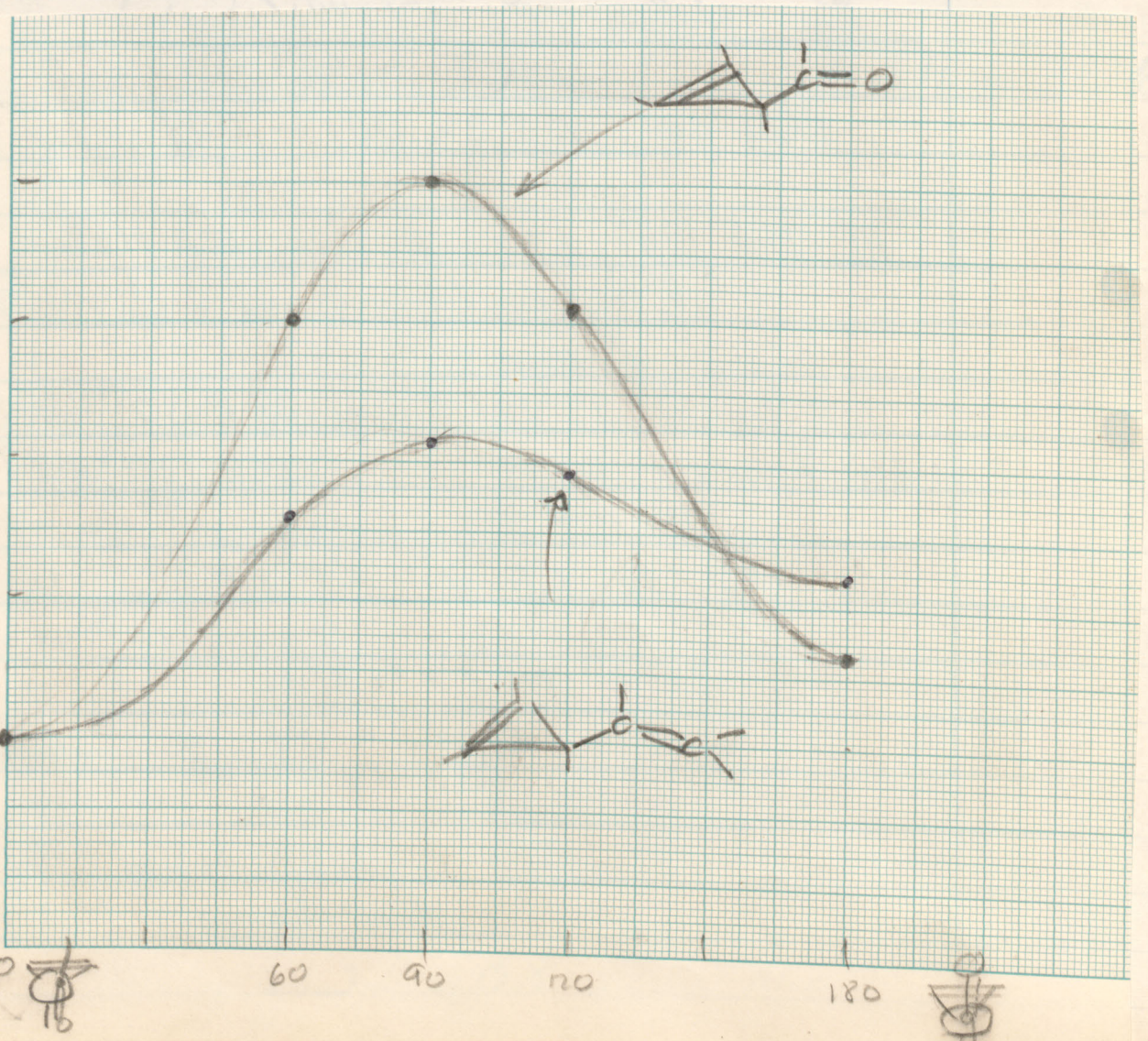




O endo	477.578	.065
60	477.333	.310
90	477.241	.402
120	477.344	.299
O exo	477.643	0

ΔE_a = 9.7 kcal in cyclopropyl

Δ = .24 ev
0-90



10 X 10 TO THE CM. KEUFFEL & ESSER CO. 358-14B MADE IN U.S.A.

Deuterium Isotope effects

✓14429.425 kcal 1.10

1.099	C-H$_a$ + e	.458	330	
	a	.443	18	
	e	.440	15	
1.096	a+e	.551	126	
	a	.492	67	
	e	.487	62	
			129	
2-a, carbonium ion				
1.100		✓13751.038	0	67.8. 387
1.099	a+e	.0 .078	40, 7	.380
	a	.064	28 8	.379
	e	.051	13 less 2	.389
1.096	a+e	.198	160 34	.353
	a	.143	105 38	.349
	e	.093	55 −7	.394

D slows the rate in reality

$K_H/K_D > 1$

incorrect behavior

could it be fault

of 1.10 not being equal dist.?

or is my judged line

factor dominant.

\+ = more stable

− = less stable

effect felt much more in a than e

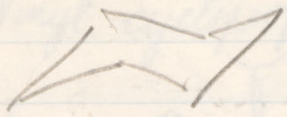
Still have to do this for trigonal

cations

i.e. shortening C_β-H has

more stabilizing effect on C^+ than

in C for a, slightly less for e



C_6H_{12}	1.10	14654.189			
	1.096 a	.385			
	e	.373			
$C_6H_{11}^+$	1.10	13942.401	711.788		
	1.096 a	.623	.762	+.26	
	e	.578	.795	−.07	

so that doesn't do it well at all. it was 38 and -7

it still has axial shortened stabilizing e^+ more than it does CH relative to 1.10

We just have found at equilibrium distance.

G. Porter - B. Ward PCS 1964, 288

ϕ. spectr ρ-C_6H_yF 17.440 cm^{-1}

$_m C_6H_yF$ 18.530

assigns σ as $\pi \to \pi$. $_o C_6H_yF$ 16.080

Ethane $\zeta = 1.3$

C-H	1.10	248.088	1.05			1.00	249.113
	1.09	248.212	1.04			.99	249.186
	1.08	248.332	1.03	248.859		.98	249.254
	1.07	248.447	1.02	248.949		.97	249.315
	1.06		1.01	249.033		.96	249.371
						.95	249.420
86	.551	.8869 ethan	.90	249.565	.8732	.94	249.462
85	.529	.8900	.89	.57280$_3$	.8768	.93	249.498
84	.497	8930	.88	.57325$_1$	.8803	.92	249.527
83	.458	8959	.87	.5660	.8836	.91	249.549
ν	.411	.5981					

Doenna

H. Howard + Ow King; (87) Can. J. Chem 37, 700 (1959)

Acetylene:

b_g — Π_g

a_g

b_u — Π_u

a_u

Walsh + I have, I think $a_u^2 b_u b_g$ correl → Δ_u

but Mulliken, Ross. have $a_u b_u^2 a_g$ correl → Σ_u^-

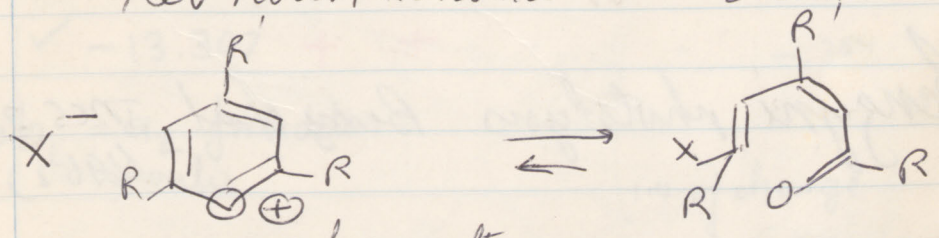
corresponding as states are a_2

Howard + King a_u is $a_u b_u^2 a_g$ ✓

I really haven't looked at that state, but I suppose at

for $a_u^2 b_u a_g$

Rev Roum d. Chimie — Z. Simon + AT Balaban



pyrylium salts

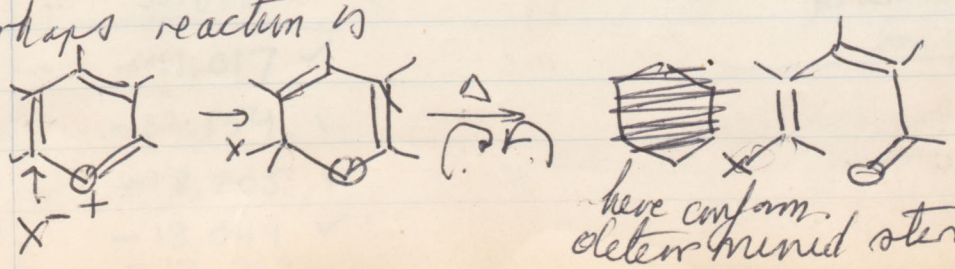
2 cis trans isomers possible but for X = CN only one

Balaban, Wiley + Crawford. JOC (in press)

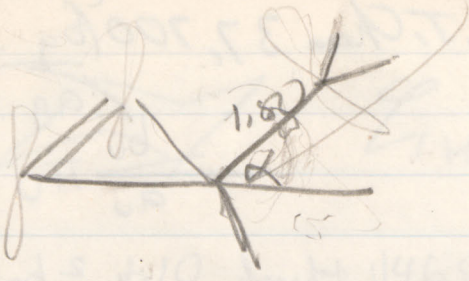
review K. Dimroth Ang. Chem. 72, 331 (1960)

see Simm Tetrah 20, 119 (1964)
O i S. 12, 22 (1962).

Perhaps reaction is



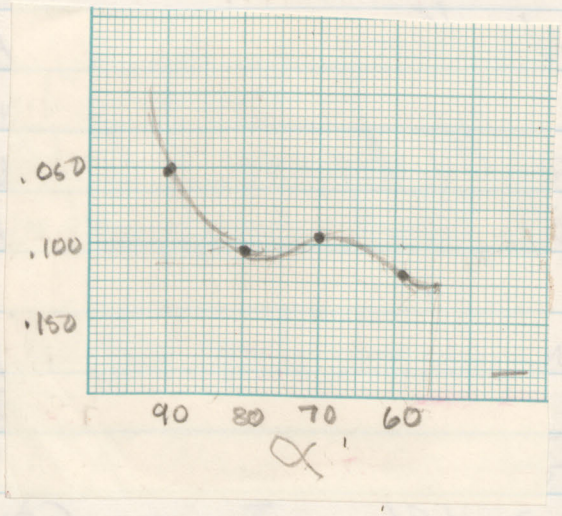
here conform determined sterically.



cyclopropenylcarbinyl bending

α = cyclopropane 60	355,119
70	355,096
80	355,104
90	355,051

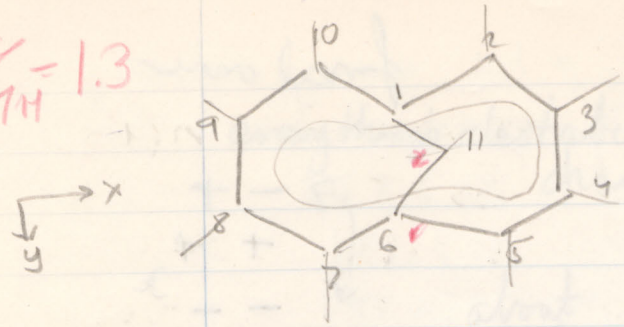
gains a little, but not much.



Benzyne photolysis Berry et al JACS 84, 3570 (1962)

Doering

$\gamma_{CH} = 1.3$



after Vogel

$C_{11}H_{10}$

1-6 = 2.178

∢ 1-11-6 = 90°

distances		
	1-11	1.54
	1-2	1.395
	2-3	1.401
	3-4	1.400

23
34
45

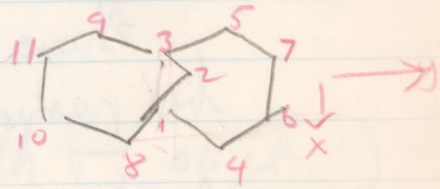
949.101

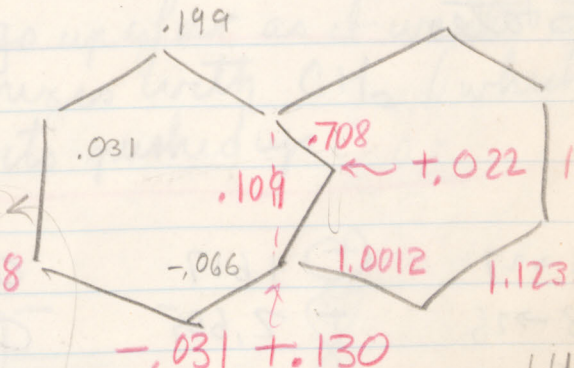
assign x assign y

			long	short		
b_2	23	✓ −5.111	−	+	−.252	
a_2	24	✓ −6.230	−	−	π	
a_1	25	✓ −7.081	+	+		
b_2	26	✓ −8.412	−	+	a^+	.230
b_1	27	✓ −9.400	+	−	a^-	
b_2	28	−11.017	−	+	−.522	
a_1	29	✓ −12.173	+	+	−.108	
a_2	30	✓ −12.205	−	−		
a_2	31	−13.044	−	−		
b_1	32	✓ −13.210	+	−		
a_1	33	✓ −13.307	+	+		

$b_2 \rightarrow b_1 = a_2$ forbidden should

CH₂ y x z





naphthalene

		long	short
	$b_2 b_{3g}$	−	±
	$a_2 a_u$	=	±
	$a_1 b_{1u}$	+	+
	$b_2 b_{3g}$	−	+
	$b_1 b_{2g}$	+	−
$^1B_{2u}$	$a_2 a_u$	−	−
	$a_1 b_{1u}$	+	+
	$b_2 b_{3g}$	−	+
	$b_1 b_{2g}$	+	−
	$a_1 b_{1u}$	+	+

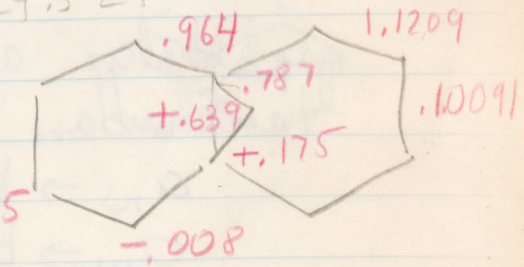
no 3,3'

1.4 of charge

949.101

919.780

29.3 21



a little more C-T to β carbons + effect in bond.

cation, trigonal at C_{11}

22	−5.111
23	−6.230
24	−7.160
25	−8.412 ✓
26	−8.948
27	−10.322
28	−11.017 ✓
29	−12.154
30	−12.205 ✓
31	−13.044 ✓
32	−13.339

$+ b_{3g}$

naphthalene 3-3′ bonding

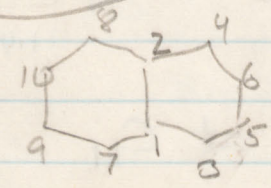
ℓ	s		final order
−	−	○	− +
+	+	+	+ +
−	+	−	− −
+	−	○	+ −
+	+	+	+ +

those orbitals which are 3-3′ bonding should be pushed up, destabilized; opposite of what happens ?

States

					naphth. gaps
28→27	1.617	a_2	×		
28→26	2,605	a_1	←	A_{1g} (−+)→(−+)	5.037
29→27	2.773	b_1	←	B_{3U} (++)→(+−)	{3.358 3.825
30→27	2.805	b_2	←	B_{2U} (−−)→(+−)	2.735
29→26	3.761	b_2	←		4.448
(28→25	3.936	b_2	←	$\sigma \to \pi^*$ 3.6	
30→26	3.793		←		

my naphthalene



		ℓ	s	
b_{3g}	−3.348	−	+	↓
a_{1U}	−6.228	−	−	n.g.
b_{1U}	−7.368	+	+	l.c
b_{3g}	−8.248	−	+	l.c
b_{2g}	−9.338	+	−	l.c
a_{1U}	−12.073	−	−	l.c
	−12.362 σ		− −	
	−12.615 σ		+ +	
b_{1U}	−12.696	+	+	
b_{3g}	−13.285	−	+	
b_{2g}	−13.919	+	−	
b_{1U}	−14.865	+	+	

naphthalene allowed transitions are

$a_{1U} \to b_{2g} = b_{2U}$

$a_{1U} \to b_{3g} = b_{3U}$

but $b_{1U} \to b_{2g}$ also $\to b_{3U}$ — one allowed, one forbidden in alternant approx

B_{3U} exper. weak, below B_{2U}

≃4 ev ≃ 3100 Å f≃10⁻⁴ ≃ 4,5 ev ≃ 2800 Å

everything's destabelized; except $\begin{matrix}--\\+-\end{matrix}$, which are changed very little because they have no 3-3' content

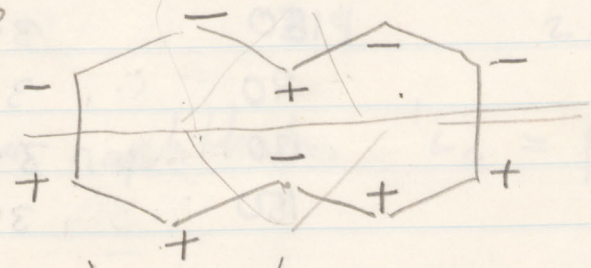
about $++$ vs $-+$; maybe its reasonable that antibonding orbital changes most, as distance is changed

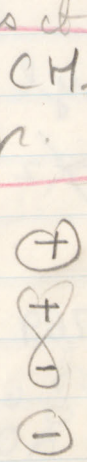
look at change of bonding on a_2 excitation

(Really $++$ mixes with σ, so it can't go up as far as it wants.)

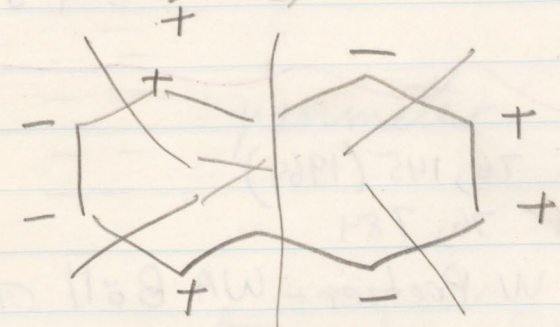
also $-+$ mixes with CH_2 (which is "below" so its pushed up.

28





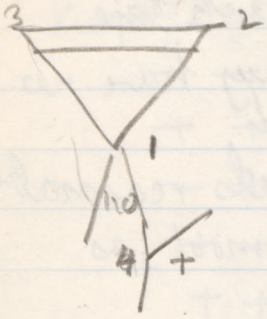
27



28→27 break bridge bnd
lengthen $\alpha-\beta$
shorten $\beta-\beta'$

11.0
12.2
12.2
12.6
12.7
13.3

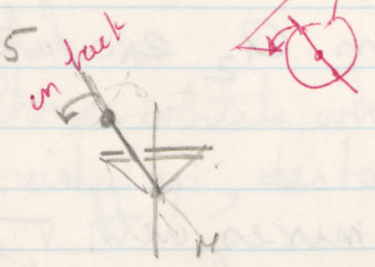
cyclopropenyl carbengl $\zeta_H = 1.3$ going nonclassical



20° rot

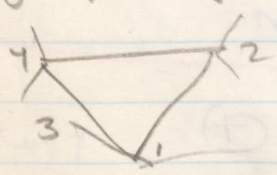
		n(3-4)	(1-3
0° ecl	357.522	−.0361	.4893
30	357.191	−.0755	.5288
60	356.701	−.0877	.5746
90	356.647	−.0205	.5448
120	357.105	.0167	.4943
150	357.484	.0008	.4747

357.665



looks like a minimum
150 → 180
more in direction pointing toward a

cyclopropyl



393.769

20° rot

		3-4	1-3
0° from ecl H	393.517	−.0254	.5491
30	393.242	−.0616	.5936
60	392.896	−.0715	.6369
90	392.866	−.0279	.6118
120	393.194	.0103	.5532
150	393.460	.0057	.5321

E. Vogel + HD Roth AC 76, 145 (1964)
E. Vogel + WA Böll AC 76, 784
E. Vogel, M. Biskup, W. Pretzer + WA Böll 76, 785

F Sondheimer E. Shani, JACS 86, 3168 (1964)

says Halbrooner is looking at spectrum of 1

maxim	256	ε = 68000	log ε = 4.8
	259	63000	
	298	6200	3.8

long wavelength band 8 maxima 350 → 400 mμ
ε = 95 → 185
≃ 2.00

O compound has maxim 257 ε = 74600
302 7100
16 maxima 345 → 435 ε = 50 → 300

X = N — $COCH_3$ 252 ε = 57000
299 5300
387 300
398 500
408 570

benzene 193 → 204 ε = 8000
230 → 270 str. ε = 230

			eV
naphthalene	220	log ε = 5.5	5.63
	275	3.75	4.51
	314	2.50 sh	3.97

m naphthalen $^1L_a = \rho = B_{2u}$ band
≈1400 Å

oct 4
calc. 2.7 1.6

perimeter

So spectrum does look like that of simple naphthalene, red shifted

I would get B_{3u} red shifted
B_{2u} fixed
new band (A_{1g}) in
low λ $b_{3g} \rightarrow b_{2g} = b_{1g}$?

acetylene

C_{2v} cis			C_{2h} trans		
173.781			175,293		
-8.636	(π)	a_2	8,636	(π)	b_g
-10.968		b_2	9.937		a_g
-12.397		a_1	13.079	(π)	a_u
-13.079	(π)	b_1	13.845		b_u

$b_1^2 a_1 b_2 = B_2$ 172,362 — $b_u^2 a_u a_g = A_u \leftarrow {}^1\Sigma_u^-$ 172,152

$a_1^2 b_1 b_2 = A_2$ 171,671 — $a_u^2 b_u a_g = B_u$ 171,385

$b_1^2 a_1 a_2 = A_2$ 170,020 — $b_u^2 a_u b_g = B_u$ 170,851 $\leftarrow {}^1\Sigma_u^+$

$a_1^2 b_1 a_2 = B_2$ 169,339 — $a_u^2 b_u b_g = A_u$ 170,884

${}^1\Sigma_u^-$, ${}^1\Delta_u$ — ${}^1\Delta_u$, ${}^1\Sigma_u^+$

linear ground 176.245
excited 171.803

thus $A_u = b_u^2 a_u a_g$ trans bent $(A_2, a_1^2 b_1 b_2)$
$B_2 = b_1^2 a_1 b_2$ cis bent $(B_u, a_u^2 b_u a_g)$

+ in one electron energy the B_2 state is lower

for $B_2 - B_u$ Howard + Kuhn CI
17.65 (10.24) 14.18 (6.70)

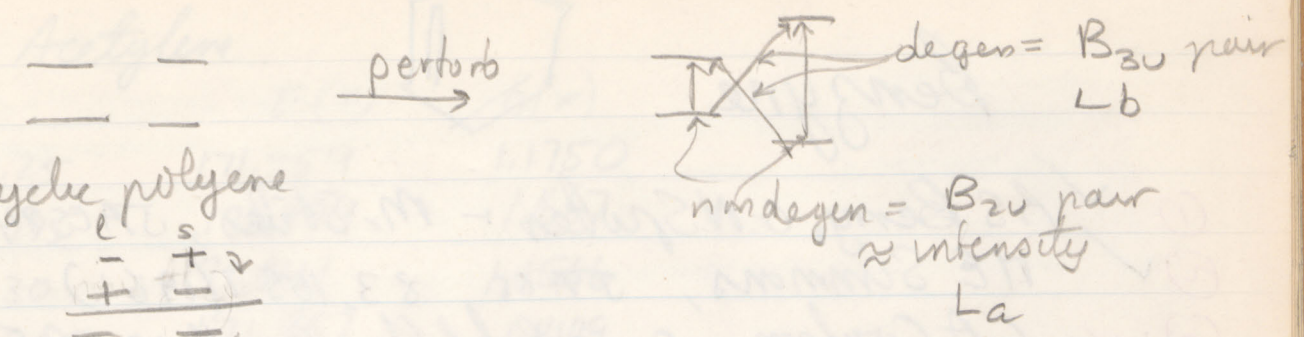
ground st at 1.21 Å 178,197
exc 171.86 !

only 6 electron problem

$b_1 + b_2$ interchanged before CI

A_u trans < lin < cis
after CI B_u lin < ~~trans~~ < ~~cis~~ same B_2
B_u trans < cis < lin

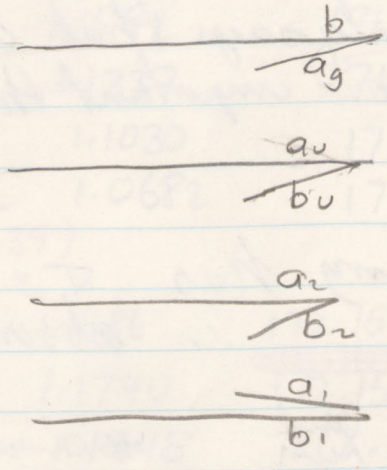
(A₂) ${}^1\Sigma_u^-$: A_2



$\equiv$ general red shift of B_{3u}
little shift of B_{2u}

↓ also get − + coming up over all.

C_2H_2



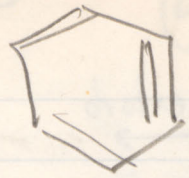
trans
$A_u = b_u^2 a_u a_g$
$B_u = b_u a_u^2 a_g$
linear

A_2 $b_1 a_1^2 b_2$
vs B_2 $b_1^2 a_1 b_2$
↑ cis

acetylene gmw

	1.188	1.208
C–H	1.08	1.058
	120.2	180

Benzyne



(1) ✓ R S Berry, G. N. Spokes + M. Stiles, JACS 84, 3570 (1962)
(2) ✓ H E Simmons, JACS 83, 1657 (1961)
(3) ✓ C A Coulson, Spec. Publ. Chem Soc. # 12, 85 (1958)

reviews: R Huisgen in Organometallic chem ed Zeiss 1960, p. 36

(4) J F Burnett, J Chem Ed 38, 278 (1961)
H. Heaney, Chem. Rev. 62, 81 (1962)
R. Huisgen + F. Sauer, Angew 72, 91 (1960)

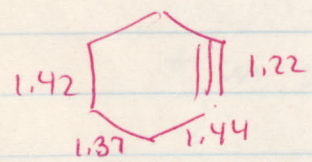
Simmons only says that covalent structure is more important than ionic

Berry has $\pi \to \pi^*$ between π levels.
∴ absorption maybe such

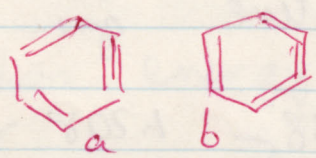
Schaller + Lutz 3400 → 4400 Å emission continuum

Berry observed transient continuum ~ 2400 $\tilde{\nu}$
$\epsilon < 100$

(3) estimated bond lengths by deviation procedure



says ↗ indicates π only calcul.



a predominates over b

(Kurz) Sargold says benzyne is like excited as acetylene.
not really

Doering

(97)

Acetylene

		E(*)	n(*)
linear	1.25	171.759	1.1750
	1.275	171.809	1.1667
	1.30	171.841	1.1566
	1.325	171.857	1.1449
	1.35	171.859	1.1318
	1.375	171.846	1.1173
	1.40	171.822	1.1017
	1.425	171.787	1.0850
	1.45	171.741	1.0673

~1.389 for bondorders
(avg 1.39)

		trans (B u)		cis (	
170°	1.25	171.778	1.1785	171.821	1.1873
	1.30	171.860	1.1592	171.891	1.1660
	1.35	171.878	1.1337	171.899	1.1391
	1.40	171.842	1.1030	171.855	1.1074
	1.45	171.762	1.0682	171.770	1.0719
		(1.39)		(1.385)	
150°	1.25	171.848	1.1986	172.156	1.2598
	1.30	171.932	1.1740	172.156	1.2229
	1.35	~~171.956~~	1.1441	172.111	1.1838
	1.40	171.930	1.1098	172.028	1.1426
	1.45	171.863	1.0720	171.913	1.0995
		(1.385)		(1.37₂)	
120	1.25	171.214	1.2078	172.030	1.3453
	1.30	171.358	1.1761	171.981	1.2916
	1.35	171.446	1.1403	171.899	1.2377
	1.40	171.486	1.1011	171.792	1.1835
	1.45	171.487	1.0592	171.663 (1.35	1.1292

Au state has a minimum for cis form wrt linear as well.

Au (cis)	170°	150°	120°
1.25	171.786	171.851	170.983
1.35	171.875	171.898	171.138
1.45	171.753	171.766	171.131

Bu state has no minimum for trans form; wants to be strictly as.

RESEARCH

10 Pi Electron System Is Aromatic

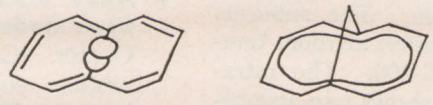
West German chemists develop structure and aromaticity of 1,6-methanocyclodecapentaene

Chemists at the Institut für Organische Chemie at the University of Köln (Cologne) have woven an impressive fabric of evidence substantiating the aromatic character of 1,6-methanocyclodecapentaene (1,6-MCDP) and confirming the presence of a delocalized system of 10 pi electrons [*Angew. Chem.*, **76**, 784, 785, 786 (1964)]. The German chemists revealed synthesis of the cyclodecapentaene earlier this year and have since spent their time in establishing structure and properties and in studying substitution reactions.

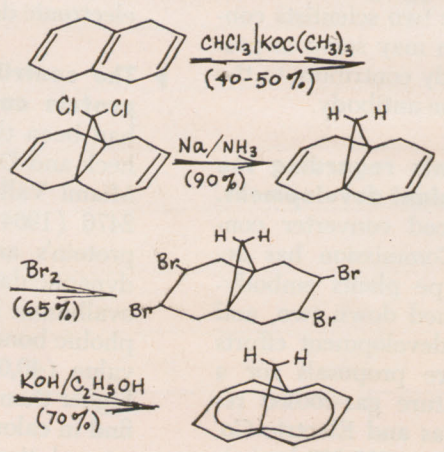
The work thus confirms, for the 10 pi electron system, the Hückel rule that monocyclic planar polyenes having 4n + 2 pi electrons (where n is an integer) should be aromatic. And, according to Prof. Dr. Emanuel Vogel, head of the institute and driving force behind the work, "Fascinating chemistry will emerge from 1,6-MCDP and related compounds." In this connection, he points to the relative abundance of 1,6-MCDP (about 200 grams have been made so far at the university).

The novel 10 pi system can be looked upon as a derivative of cyclodecapentaene, Prof. Vogel says. Its synthesis complements the previous preparation of the cyclononatetraenyl anion by Dr. Thomas J. Katz and coworkers at Columbia University and Dr. E. A. LaLancette and Dr. R. E. Benson at Du Pont.

Cyclodecapentaene itself, as indicated by models, cannot attain planarity (a prerequisite for effective delocalization of the pi electrons) because of serious overlap of the van der Waals radii of the 1,6-hydrogen atoms at the trans double bonds. Isomerization to 9,10-dihydronaphthalene would seem to be an obvious way for the molecule to evade this steric compression, Prof. Vogel says. Recent work on 9,10-dihydronaphthalenes done independently by Dr. E. E. van Tamelen of Stanford University and Prof. Vogel gives experimental support to this view. However, the Cologne group reasoned that exchanging a methylene bridge for the two internal hydrogen atoms in cyclodecapentaene might flatten the 10-membered ring enough to permit delocalization.



Synthesis. The synthesis of 1,6-MCDP, a faintly yellow solid melting at 28° to 29° C., is straightforward. The starting material is 1,4,5,8-tetrahydronaphthalene. The reaction sequence involves as a crucial first step the highly selective addition of dichlorocarbene, generated from chloroform and potassium-*tert*-butoxide, to the central double bond of the tetrahydronaphthalene.



The true nature of 1,6-MCDP wasn't immediately clear. Three possible structures had to be considered:

- Tricyclo[4.4.1.$0^{1,6}$]undeca-2,4,7,-9-tetraene—that is, the 9,10-dihydronaphthalene type of isomer of 1,6-MCDP containing a three-membered ring.
- An olefinic 1,6-MCDP with oscillating double bonds similar to cyclooctatetraene.
- 1,6-MCDP with a highly delocalized 10 pi electron system.

It is this third structure that has proved to be the correct one.

Nuclear magnetic resonance and ultraviolet spectra and chemical behavior helped the West German chemists to work out the structure of 1,6-MCDP and demonstrate the compound's aromaticity.

The NMR spectrum shows an A_2B_2 system (eight ring protons) at 2.5 to 3.2τ, centered at 2.8τ, and a sharp signal at 10.5τ (two protons of the bridge methylene). Absorption of the olefinic protons at low field (in the aromatic region) combined with the strong shielding of the methylene protons above the ring indicates the presence of a ring current. These NMR findings, Prof. Vogel says, are in line with recent work on the related 14 pi electron system, *trans*-15,16-dimethyldihydropyrene, by Dr. Virgil Boekelheide and Dr. Joseph B. Phillips of the University of Oregon, and work on 14- and 18-membered aromatic annulenes by Dr. Franz Sondheimer and co-workers at Israel's Weizmann Institute of Science.

Also, low-temperature NMR spectra (down to −145° C.) measured by Dr. Joseph B. Lambert of California Institute of Technology show no change. This observation argues against the olefinic structure with oscillating double bonds.

Finally, NMR analysis gives a C^{13}–H^1 coupling constant for the bridge methylene hydrogen atoms of 142 cps. This value tallies with the $C–CH_2–C$ bond angle of about 90° which the Cologne chemists infer from models of 1,6-MCDP. If a cy-

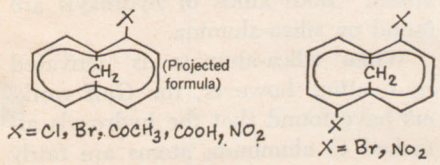
clopropane ring were present, the expected C^{13}–H^1 coupling constant would be about 160 cps. Thus, Prof. Vogel says, "All the NMR data fit together nicely."

UV data also support the proposed structure. The UV spectrum shows absorption bands with maxima at 256 mμ. (extinction coefficient of 68,000), 259 mμ. (extinction coefficient of 63,000), and 298 mμ. (extinction coefficient of 62,000) and a low intensity band of some eight maxima reaching into the visible range (350 to 400 mμ. with extinction coefficients of 95 to 185). There is apparent similarity to the UV spectrum of naphthalene.

The chemical behavior of 1,6-MCDP fully bears out the aromatic character indicated by the spectral data:

- The compound shows no tendency to polymerize at room temperature and isn't sensitive to air.
- Refluxing in benzene solution with maleic anhydride gives no reaction.
- Reaction with electrophilic reagents gives mono- and disubstituted 1,6-MCDP's. (NMR and UV spectra show that the cyclodecapentaene skeleton is retained).

Substitutions. The substitution reactions already tried at Cologne involve halogenation, acetylation, nitration, and deuteration. Substitution products obtained either directly or by subsequent transformations are of this type:



Reaction with one mole of *N*-bromosuccinimide, for example, gives a yellow monobromide in 92% yield. (Adding bromine at −10° C. leads to the same product in slightly lower yield.) With excess *N*-bromosuccinimide, a crystalline dibromo compound forms in 40% yield. Preliminary x-ray analysis by Prof. J. D. Dunitz (of Eidgenoessische Technische Hochschule, Zurich) shows that the bromine atoms are at C-2 and C-7. From this, the German workers assume that the bromine atom in the monobromide is at C-2. The monobromide can be readily converted to the Grignard compound, which can then be carboxylated to give the corresponding acid in 80% yield.

There is some indication that substitution with bromine may proceed through addition-elimination, Prof. Vogel says. He infers this from the fact that, at −75° C., a tetrabromo adduct forms as the main product. From NMR spectra, he has tentatively assigned a cyclopropane structure to this adduct. Treating this compound with base eliminates two moles of hydrogen bromide, and gives a mixture of 2,7-dibromide and a dibromide that he presumes to be the 2,10-isomer.

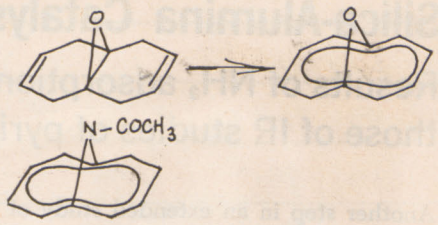
Acetylation with acetic anhydride and tin tetrachloride gives an excellent yield of a monoacetyl derivative. This compound must also have the substituent at C-2, since it can be converted to the same carboxylic acid as the bromide using NaOBr.

Nitration with copper(II) nitrate in acetic anhydride yields a liquid mononitration product that's probably a mixture of the 2- and 3-nitro compounds plus a crystalline dinitro compound. NMR spectra show that the dinitro compound corresponds to the 2,7-dibromo substitution product.

Repeated treatment of 1,6-MCDP with deuterated trifluoroacetic acid in ether in the presence of catalytic amounts of D_2SO_4 leads to tetradeuteration in the cyclodecapentaene system. The NMR spectrum of the deuterated product suggests that deuterium enters into the positions adjacent to the bridge—in keeping with the other substitution reactions.

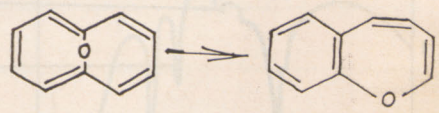
So far, the Cologne chemists haven't been able to make direct substitution at the methylene bridge. However, they hope to produce 1,6-MCDP compounds containing substituents in the bridge by introducing these substituents at an earlier stage of synthesis. Interest in such compounds stems from the fact that the substituents are located in an unusual electronic environment which may cause anomalous chemical behavior.

The German chemists have extended their synthetic scheme leading to 1,6-MCDP to the preparation of other 1,6-bridged cyclodecapentaenes. They have succeeded in replacing the methylene with oxygen and nitrogen (as $-NCOCH_3$).



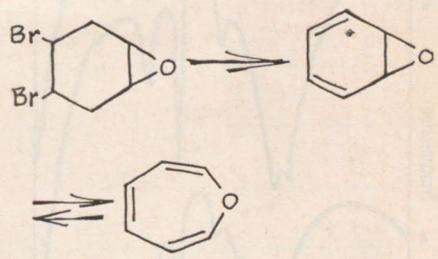
To make the oxygen-bridged cyclodecapentaene, they brominated the known epoxide of tetrahydronaphthalene, then dehydrobrominated the resulting tetrabromide with potassium-*tert*-butoxide in ether at −10° C. (60% yield in the last step). The acetylimino-bridged compound was prepared from the aziridine corresponding to the epoxide.

These heteroatomic bridged cyclodecapentaenes are not only subject to substitution reactions, but also are prone to undergo what Prof. Vogel calls intriguing molecular rearrangement. The oxygen compound, for example, when chromatographed on silica gel at room temperature, isomerizes to 1-benzoxepin:



The 1,6-oxygen-bridged cyclodecapentaene has also been described by Israel's Dr. Sondheimer.

Synthesis of the 1,6-oxygen-bridged cyclodecapentaene suggested a general approach to previously unknown oxepins by dehydrohalogenation of 1,2-epoxy-4,5-dibromocyclohexanes.



In fact, oxepin itself and its 2,7-dimethyl derivative can be synthesized by this scheme. The temperature dependence of the NMR spectrum of oxepin prompts the German workers to think it is in equilibrium with its valence tautomer (benzene epoxide). The 2,7-dimethyl derivative is free of tautomer. Only olefinic properties have been found for the 8 pi electron system oxepin.

140°

	trans		cis	
1.25	171.802	1.2079	172.275	1.2986
1.30	171.895	1.1802	172.242	1.2541
1.35	171.931	1.1478	172.171	1.2086
1.40	171.918	1.1114	172.069	1.1621
1.45	171.865	1.0719	171.940	1.1145

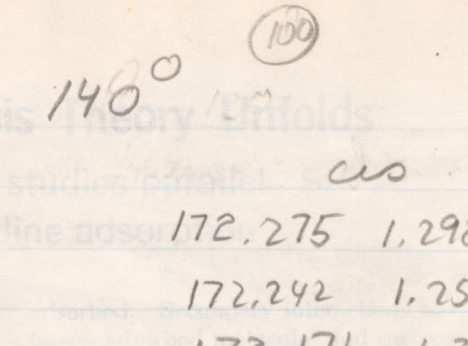
130°

1.25	171.615	1.2118	172.257	1.3286
1.30	171.727	1.1817	172.205	1.2783
1.35	171.783	1.1472	172.120	1.2277
1.40	171.792	1.1091	172.008	1.1767
1.45	171.761	1.0682	171.873	1.1254

---

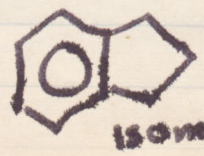
to compare propylene

allyl calim



still change in bond length 1.54 → 1.50 ∴ propylene - unsym. allyl 28.744

propyl - sym allyl 28.752

incidentally  777.123

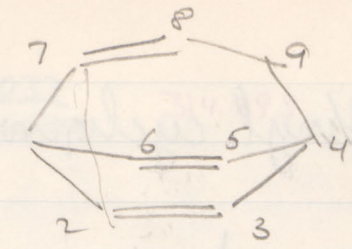
isomeric $C_9H_9^+$

but rearr. involves double H shift

(101)

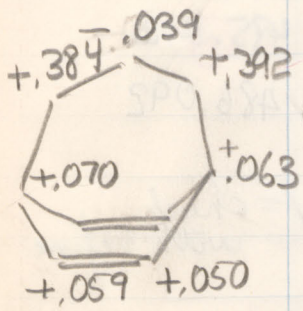
Bicyclo[3.2.2]nonatriene + 7 cation

after Dauben



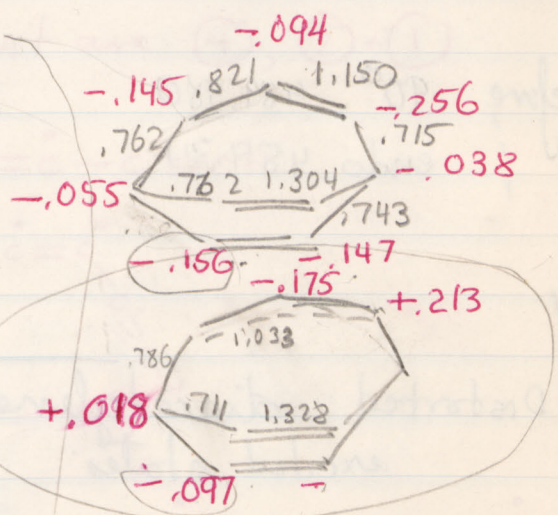
C_9H_{10}

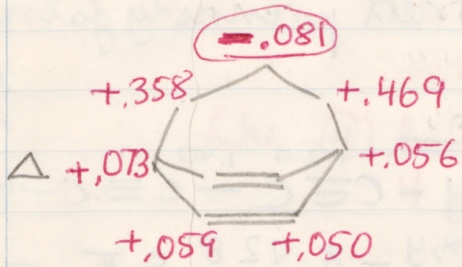
$C_9H_9^+$



(1) Symmetrical bridge 7-8 = 8-9 = 1.45 Å

RH_7	-802.127
R^+	-774.720
	27.407





note RH wants to be asym
R^+ sym.

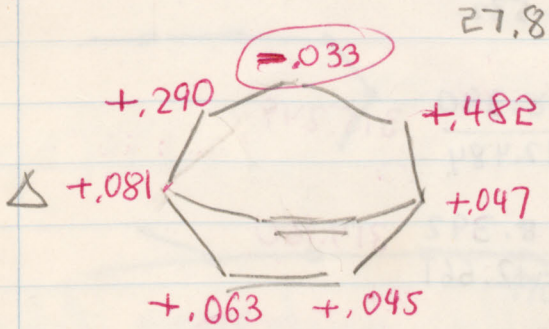
(2) Unsymmetrical bridge

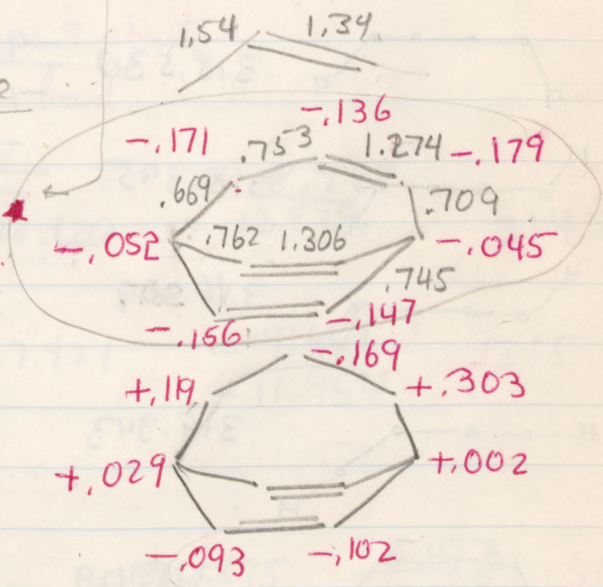
RH_7 ↗ 802.469

R^+ ↙ 774.634

27.835

$RH_{unsym.br} - R^+_{sym}$ = 27.749





bond orders unsym

	7-2	7-3	8-2	8-3	9-2	9-3
RH	-.0547	-.0191	-.0116	-.0152	-.0185	-.0415
R^+	-.0194	-.0354 ?	-.0132	-.0163	-.0250	-.0190

in R^+ $p_y(7)$ with

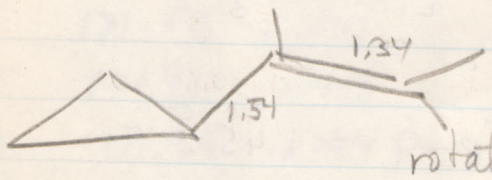
$p_z(2)$	-.0028
$p_z(3)$	+.0071
$p_y(8)$	.3240
$p_y(9)$	.0117

looks like system is gaining something over allylic stabilization.

Nov. 13

Nov. 13, 1964 (102)

Vinyl cyclopropane, torsional barrier



rotate 90° =< $\frac{8,093}{12.470}$ 489.519 ✓ 485.142

$\frac{-9,954}{-10.489}$ 486,627 486.092

2,892

✓ = check with before

before 90° 489.380

endo 489.311

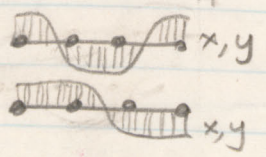
ethylene itself calc 3.5 ev.

~.6 ev saved

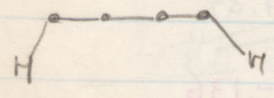
had tried previously fulvene

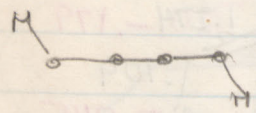
Δ = 5.2 ev

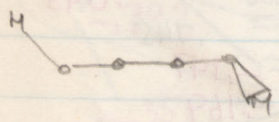
Distorted diacetylene excited states

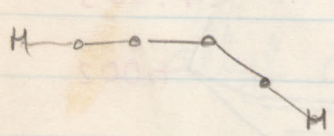


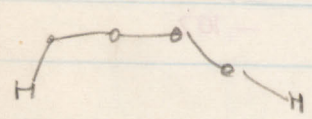
$\frac{-8.428 \text{ e}\pi}{-12.908 \text{ e}\pi}$ 320.943 316.463

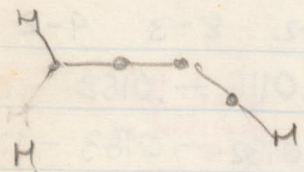
①  318.530 $\frac{-9,368}{-12,908}$ π 314.990

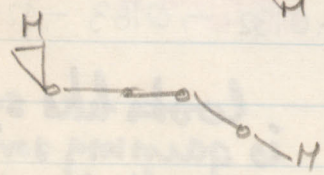
②  318.395 $\frac{-9.489}{-12,600}$ 315.284

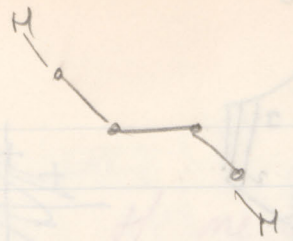
③  316.309 $\frac{-9.658}{-12,532}$ 313.435

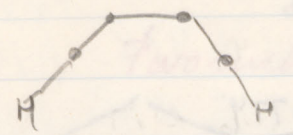
④  319.343 $\frac{-8,390}{-12,484}$ 315.249

⑤  318,429 $\frac{-8.392}{-12,661}$ 314.160

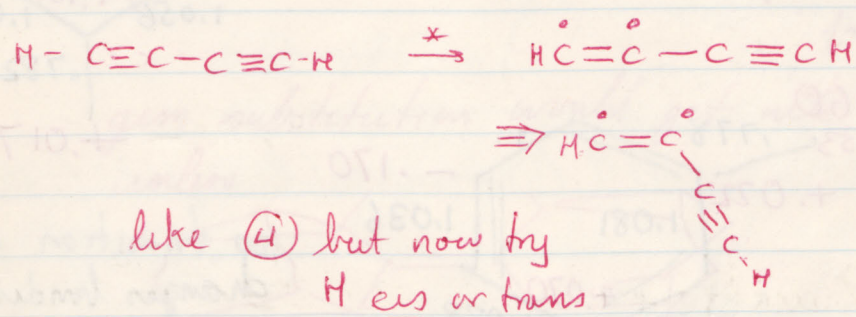
⑥  318,11 $\frac{-8.652}{-12,420}$ 314.343

⑦  318,170 $\frac{-8,825}{-12,469}$ 314,526

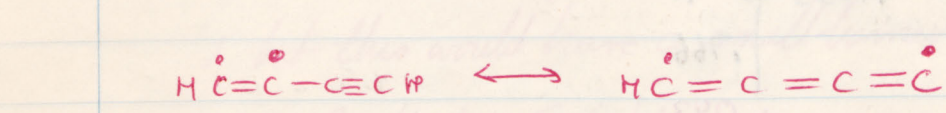
(2)  316.765 9.033 / 11.503 314.295

(9)  317.249 8.272 π / 11.850 313.671

all distortions look bad; best are (4), (2) & (1)

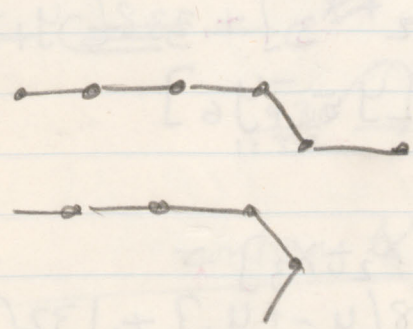


like (4) but now try H cis or trans

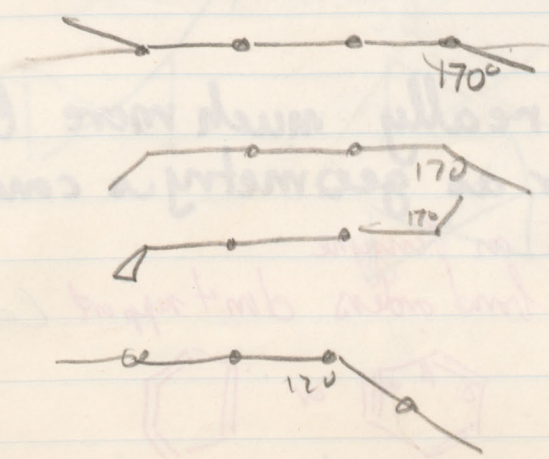


⇒ type 3 structure

but that one is bad.

 318.620 8.787 / 12.829 314.579

 317.421 −9.682 / −11.954 315.149



320.875 8.473 / 12.898 316.452

320.881 8.467 / 12.908 316.440

all bad.

320.903 8.431 / 12.898 316446

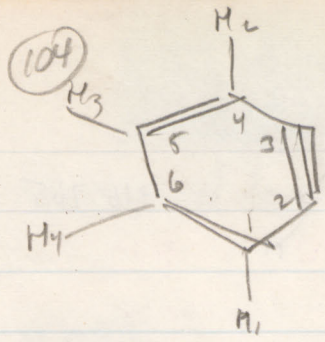
316.463

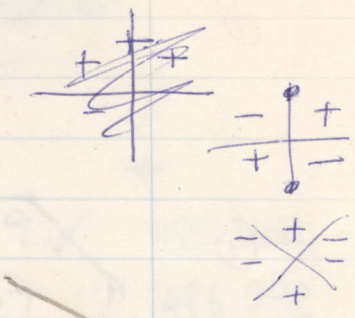
Nov. 13

(104)

Benzyne again

$q_H = 1.3$





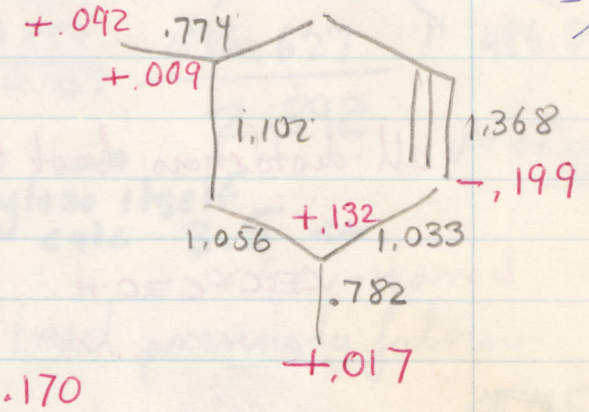
$-8.346\ \pi^* e$

$-10.194\ \sigma^*$

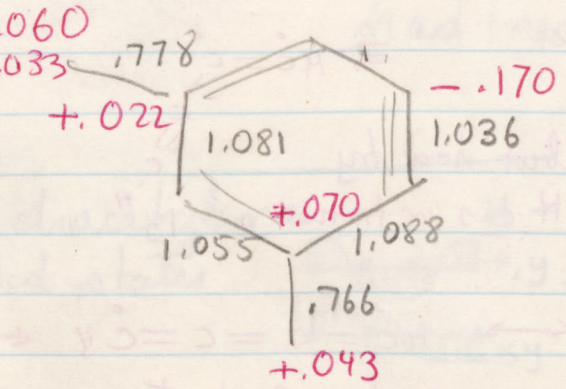
$-11.713\ \sigma$

$-12.797\ \pi\ e$

492.579



* 491.060



so transition only changes bonding at C≡C

σ^* large coeff

$-.208[S_2 - S_3] - .243[X_2 + X_3] + .238[Y_1 - Y_4]$

$-.626[Y_2 - Y_3] + .132[Y_5 - Y_6]$

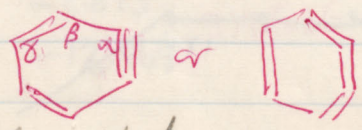
σ $-.108[S_2 + S_3] - .461[X_2 - X_3] +$

$-.411[Y_2 + Y_3] - .138[Y_5 + Y_6] + .132[X_5 - X_6]$

Excited state is really much more like benzene, as far as geometry is concerned.

Do bond variation on benzyne

buy bond orders don't support Coulson.



or

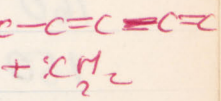
$\alpha + \beta + \gamma = 360$

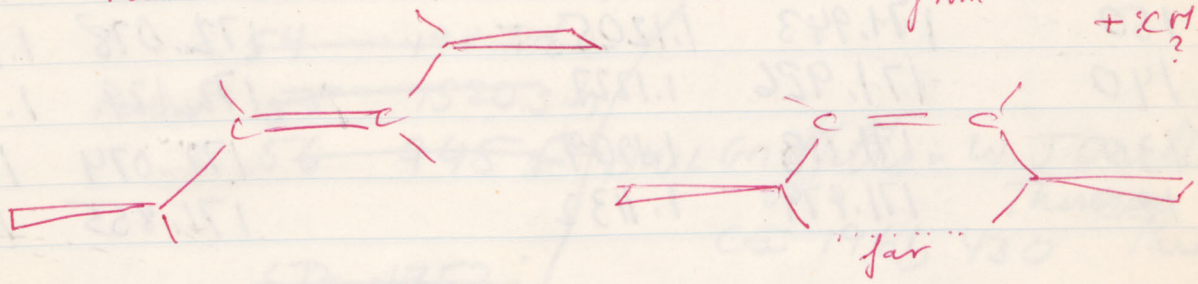
can try to get

1. α as large as possible
2. $\gamma = 120°$

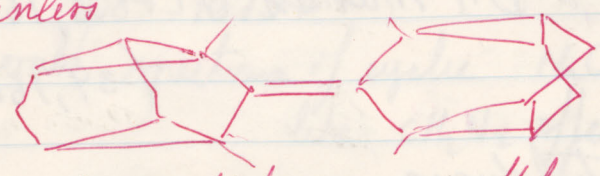
Trouble is that we need an Σ constraint

If one cyclopropane reduces C=C torsional barrier by $\frac{1}{5} \rightarrow \frac{1}{6}$

Two such should be a addition from 

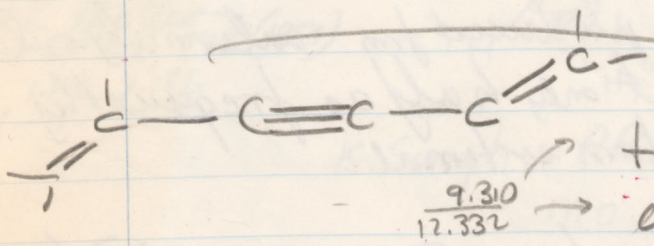


gem substitution would get into trouble unless



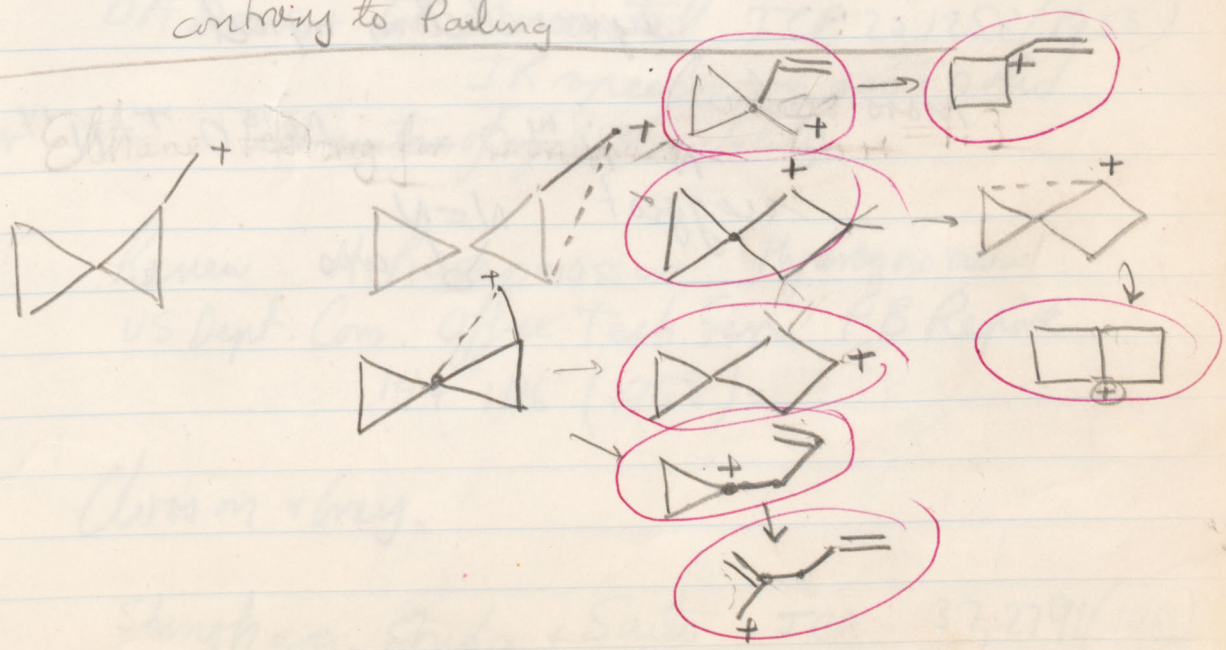
but this would have a small barrier to rotation!

Multiple Substitution easier on allene



trans	528.5669	12194.037
$\frac{9.310}{12.332}$ → cis	528.5661	12194.020
90°	528.5596	12193.870

contrary to Pauling



Nov. 13

Acetylene	1.385		1.372	
180	171.838	1.1112	171.849	1.1191
170	171.857	1.1127	171.886	1.1257
160	171.903	1.1164	171.978	1.1431
150	171.943	1.1205	172.078	1.1660
140	171.926	1.1227	172.129	1.1883 ←
130	171.793	1.1209	172.074	1.2053
120	171.479	1.1132	171.853	1.2139

JP Doering & BH Mahan JCP 36, 1682 (1962)
(34, 1617 (1961))

N_2O photolysis
cncl

in photolysis N atoms are produced from internal position, but only half as frequently as from external.

GM Begun + L Landau JCP 35, 547 (1961)
upon electron impact

mass spectra suggest $N^{15}N^{14}O \rightarrow N^{15}O^+ + N^{14} + e^-$

$N=N$
$\diagdown\ \diagup$ ons

HN_3 ~~50 15244b~~ see azides

~~49 15585h~~

~~49 2293c~~

~~44 10430a~~

~~54 1987d~~

renew ~~55 15203h~~

~~56 945f~~ Dows + Griffiths + W.J. Orville Thomas C-I 1961, 430 Thermet

~~57a 1752i~~

~~58 6305b~~ = Closson Gray

58 1075b

Howard spectrum of cyclic N_2O + HN_3 look like like CH_2N_2 effect?

N_2O

AC Douglas + CK Miller JCP 22, 273 (1954)

1.126 1.186

N—N—O

Str. E. Amble + BP Dailey JCP 18, 1422 (1950)

1.240

N=N=N

H 1.021 1.134

112°39' μ = 0.847

K. Singh PRSA 225, 519 (1954)

MO + VB calcul.

DA Dows + GC Pimentel JCP 23, 1258 (1955)

IR spectra in gas + solid

no mention of cyclic possibility

Review M. Rosenwasser Hydrazoic acid US Dept. Com. Office Tech. Serv. PB Report 144 106 (1958)

Closson + Gray

Shimokawa, Shida + Saito JCP 37, 2791 (1962)

photolysis of azides

Nov. 13

new prog. (108) 6 place

sp σ overlap is bad not good to 6 places

calculator bad

	*		to 8 pl	summing	
Ethane	.880	339 249.57	325	293	344	86,90,91,94 .94 all
	.881	371	368	344	.348	90,92
	.882	393	357	342	.347	88,95,96
	.883	406	.401	368	.392	89,94,95 2.6
	.884	412	.355	384	.349	96,87,92
	.885	410	.391	364	.391	90,91,96 2.5
	.886	400	.396	361	.374	91,89,97 2.5 m s
	.887	385	.375	355	.374	.8869992,90
	.888	359	.353	319	.342	.8879996,91,99
	.884	329	.323	320	.3	.8889997,92
	.890	289	.280	260	.269	.8899988,90,93

good to ≤ .0001 er ≤ 2 cal

Δs > 1 in 10^6

distances off by 1 in 10^{-6} Σ is off by as much as .0005 er

= =

cals good to ≈ .001 er = 23 cal

absolute accuracy ≈ 10 cal

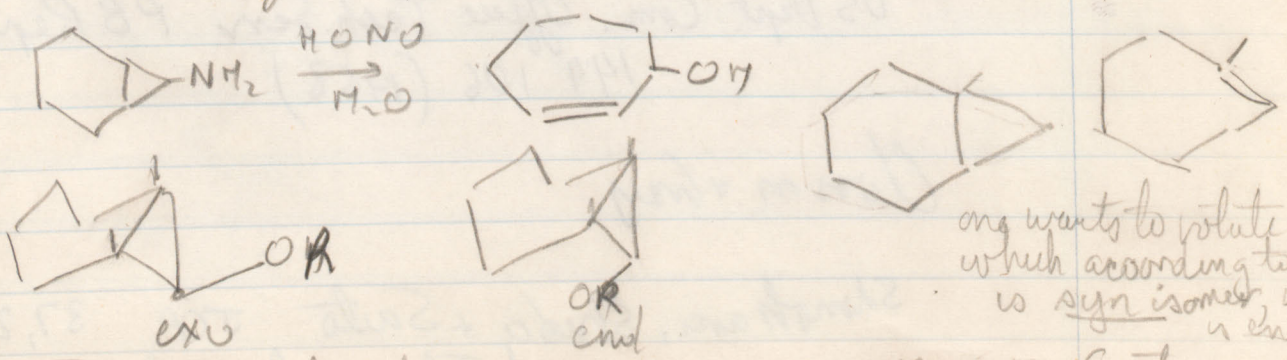
anyway distances good only to 1 in 10^{-6}

This will make it impossible to look at isotope effects!

.634 .674

so that Δ distance incorrectly predicted

J.E. Hodgkin - R.J. Flores JOC 28, 3356 (1963)



one wants to prepare ... which according to ... is syn isomer, whi... endo

(exo) R = carbobethoxy KOH → acid SOCl2 → acid chloride Curtius → amine

Doenng

(109)

C_2	2222	z	2011 2002 202	20002	2221 1	zz
1.20	1.8550	.7161	1.2209	.7553	1.6223	.8454
.22	1.8136	.7079	1.2010	.7620	1.5941	.8273
.24	1.7726	.6996	1.1811	.7676	1.5658	.8094
.26	1.7318	.6911	1.1612	.7722	1.5373	.7917
.28	1.6914	.6826	1.1413	.7760	1.5087	.7740
.30	1.6512	.6740	1.1213	.7788	1.4800	.7565
.32	1.6114	.6652	1.1014	.7809	1.4511	.7390
.34	1.5719	.6564	1.0816	.7822	1.4222	.7217
.36	1.5327	.6475	1.0617	.7827	1.3932	.7043
.38	1.4938	.6385	1.0419	.7826	1.3641	.6870
.40	1.4551	.6295	1.0222	.7818	1.3350	.6698
.42	1.4168	.6204	1.0025	.7804	1.3058	.6525
.44	1.3787	6111	0.9829	.7785	1.2765	.6353
.46	1.3410	6018	0.9633	.7759	1.2473	.6180
.48	1.3035	5925	0.9439	.7729	1.2180	.6008
.50	1.2664	.5831	0.9245	.7693	1.1888	.5835
.52	1.2295	.5736	0.9053	.7653	1.1595	.5662
.54	1.1930	.5641	0.8861	.7608	1.1303	.5489
.56	1.1568	.5545	0.8671	.7559	1.1012	.5316
.58	1.1210	.5449	0.8482	.7506		.5143
.60	1.0855	.5352	0.8295	.7449		.4970
.62	1.0505	.5256	0.8109	.7388		.4798
	1.229	1.597	1.419	1.503	1.284	1.620

353

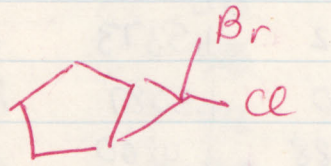
25 00

K
1.22
1.50

ΔF
119 cal
240

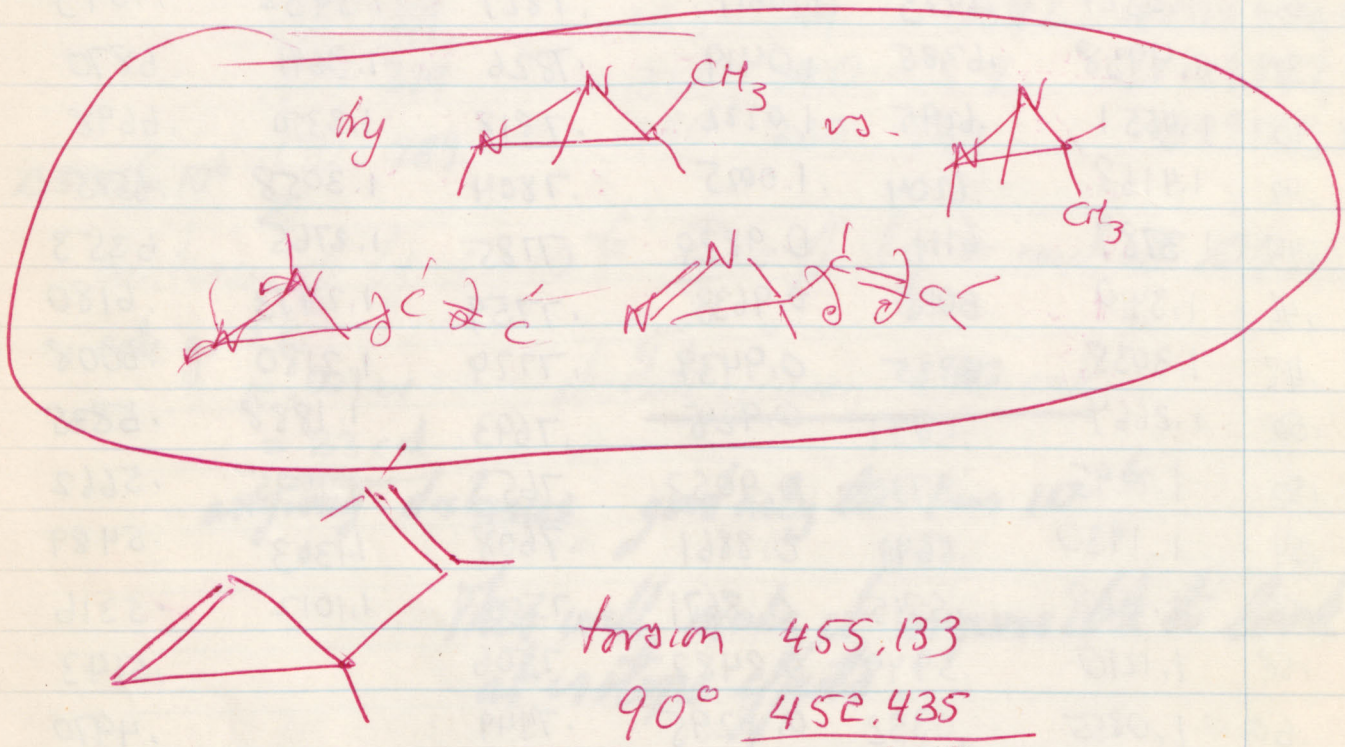
Nov. 13

P S Skell + S R Sandler
JACS 80, 2024 (1958)

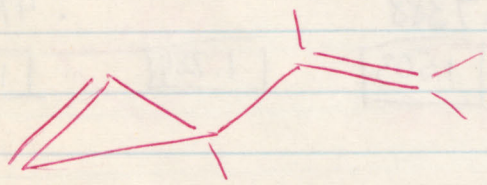


+ Ag^+ α isomer loses Cl^-
β " " Br^-

also



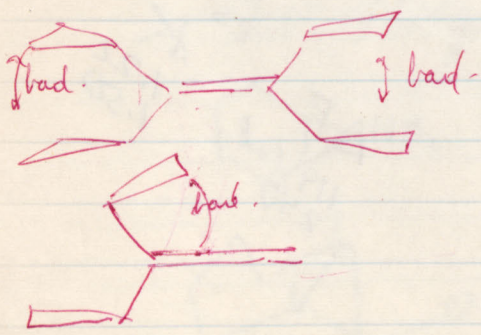
torsion 455.133
90° 452.435
2.698



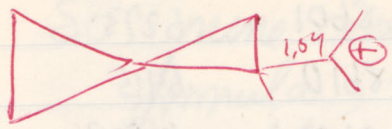
455.255
452.471
2.784

ethylene 3.5

vinyl cyclopropane 2.892
not really much better



spiropentyl carbinyl.



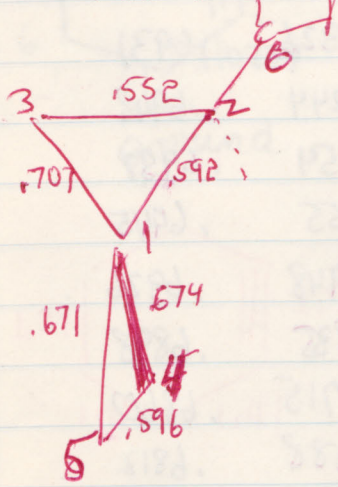
0	563.790
30	563.652
60	563.471
90	563.440
120	563.591
150	563.759

$\Delta \approx .330$ ev.

.673 m

.384 m

so it's quite like a cyclopropane.



	0°	90°
1	+.179	+.092
2	+.064	−.015
3	−.154	−.198
4	−.229	−.232
5	−.210	−.234
6	+.316	+.513

Nov. 13

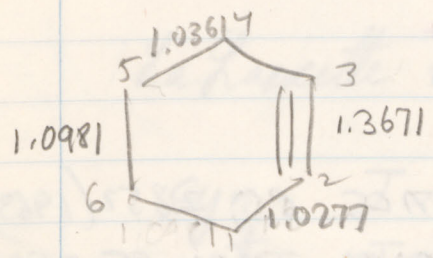
	22 2 2 22 1 12 22202	21 3 2 21212	21 41 (lr) 21221	2 2 2 11 221111	22 1 21 221021	2042 20222
1.20	1.3895	1.5772	1.8100	.8601	.6273	1.7650
.22	1.3746	1.5614	1.7810	.8610	.6415	1.7483
.24	1.3590	1.5449	1.7516	.8606	.6538	1.7307
.26	1.3428	1.5276	1.7221	.8588	.6643	1.7124
.28	1.3260	1.5097	1.6923	.8557	.6731	1.6933
1.30	1.3087	1.4911	1.6624	.8515	.6802	1.6736
1.32	1.2904	1.4721	1.6323	.8462	.6859	1.239
.34	1.2725	1.4525	1.6022	.8399	.6902	
.36	1.2537	1.4324	1.5719	.8326	.6931	
.38	1.2345	1.4119	1.5415	.8244	.6948	
1.40	1.2148	1.3910	1.5111	.8154	.6952	
.42	1.1947	1.3697	1.4807	.8055	.6945	
.44	1.1743	1.3481	1.4503	.7948	.6926	
.46	1.1536	1.3262	1.4199	.7835	.6898	
.48	1.1325	1.3041	1.3896	.7715	.6860	
1.50	1.1112	1.2817	1.3593	.7588	.6812	
.52	1.0895	1.2591	1.3291	.7456	.6756	
.54	1.0677	1.2363	1.2990	.7318	.6691	
.56	1.0456	1.2134	1.2690	.7175	.6619	
.58	1.0233	1.1903	1.2391	.7028	.6539	
1.60	1.0009	1.1672	1.2095	.6876	.6453	
.62	.9784	1.1439	1.1800	.6721	.6361	
	1.340	1.283	1.235	1.510	1.543	

	obs		obs.	Hurley	calc from fault
2	1.597	224	1.229	1.242	1.25	1.2
22	1.620	2231	1.284	{1.312 1.328}	1.30	1.3
202	1.419	2222	1.340	1.369	1.35	1.3
2002	1.503	2132	1.283	{1.266 1.273}	1.28	1.2
2		2141	1.235	1.238	1.23	1.2
.01	+.012	22211	1.510	1.535	1.54	
001	−.089	22121	1.593		1.59	
0001	−.047	2042	or 1.239	1.252	1.21	1.16

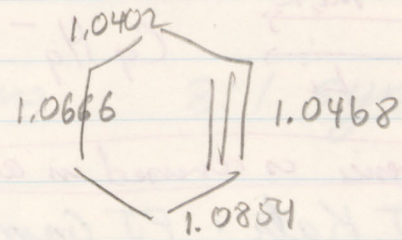
$1.597 + .012 N_y - .089 N_w - .047 N_x + .$ .11 Mullikan Hurley

1.62 1.47 .03 .01 .11 .18 .03 .01 .11 .18

So; mine considerably worse than Hurley's formula, but that is an empirical fit, while mine uses a bond order bond length curve derived from other molecules.



ground



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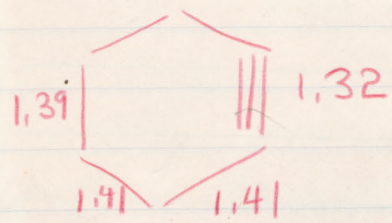
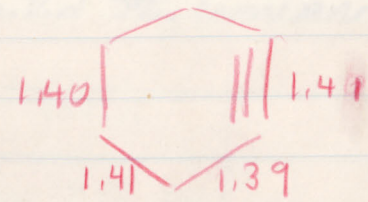
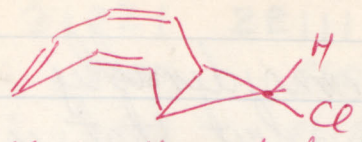




Valence tautomerisms: Review
Vogel AC 1963 begin.

Diels-Alder Review
JG Martin + RK Hill Chem. Revs 61, 537 (1961)

re synthesis of  JACS 1963

Katz thought he had one epimer
Dupont both

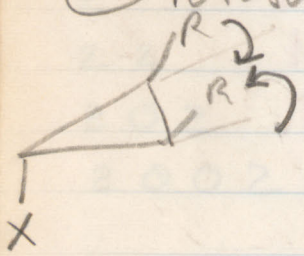
$\xrightarrow[Li]{Na,K}$ $C_9H_9^-$ K^+ Li^+

check if my preference is reversed in anion

TJ Katz + PJ Garratt JACS 85, 2852 (1963)
EA LaLancette + RE Benson, JACS 85, 2853 (1963)

	mixed	con mode only	
trig con cis	502.099	512.282	
trans	502.142	512.427	
dis cis out	502.129	512.112	steric factor dominates
in	502.024	512.146	
trans	502.107	512.194	
hole cis con cis	501.464	511.918	
trans	501.659	511.977	
dis cis out	501.269	511.877	rev
in	501.601	511.789	
trans	501.478	511.922	
hole trans con cis	501.761	511.852	
trans	501.659	511.977	
dis cis out	501.854	511.697	rev
in	501.593	511.853	
trans	501.775	511.794	

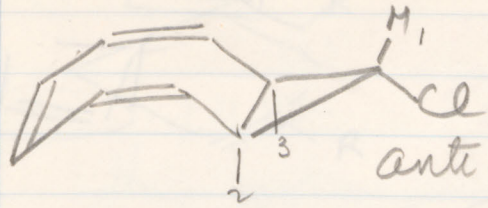
so I would say
• retains original pref.
(−) reverses.



Doering

(115)

Katz says he has X anti isomer



$J_{H_1-H_{2,3}} = 4$ cps.

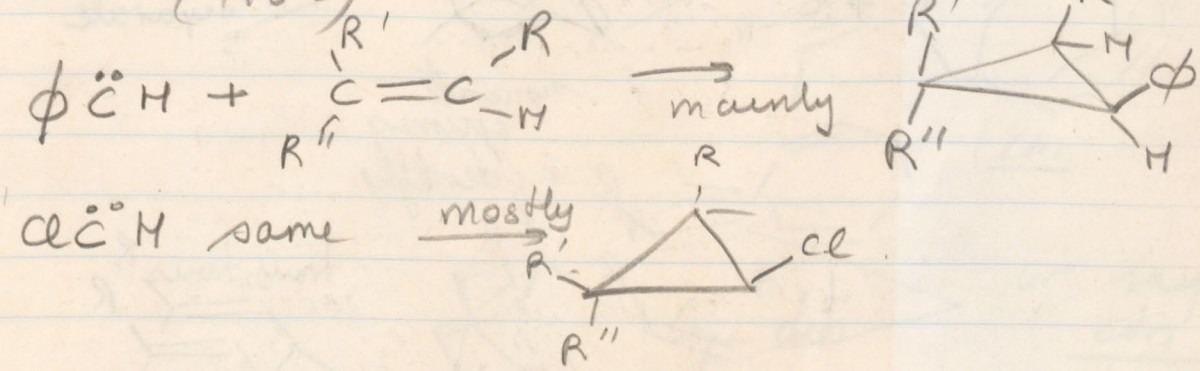
La Lancette has two 3:1 syn → anti

syn $J = 7.6$
anti $J = 4.3$

they subjected the isomeric mixture to Li dispersion.

Wrote to Benson Nov. 20 asking if epimers were separ.

See GL Closs, RA Moss, JJ Coyle, JACS 84, 4985 (1962)



It has been assumed that steric hindrance in the transition state will be product controlling
ref — Closs + Closs JACS 82, 5723
EE Schweitzer — WE Parham 82, 4085
Schöllkopf + Lehmann Tet. Let 165 (1962)
(our article)

See also Schöllkopf Tetrah Lett (241) (1962)
165
105 (1963)

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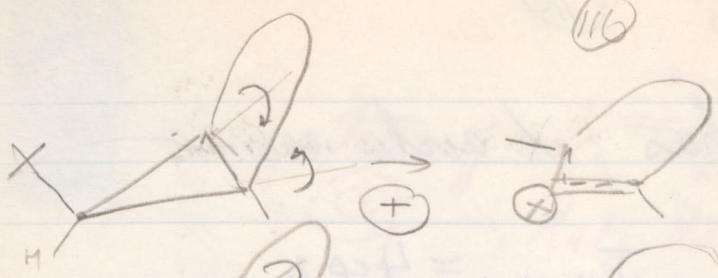
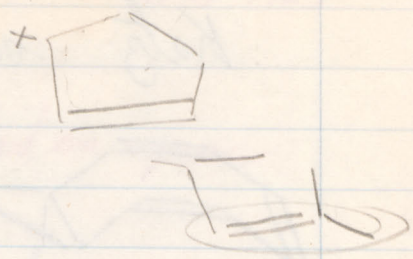
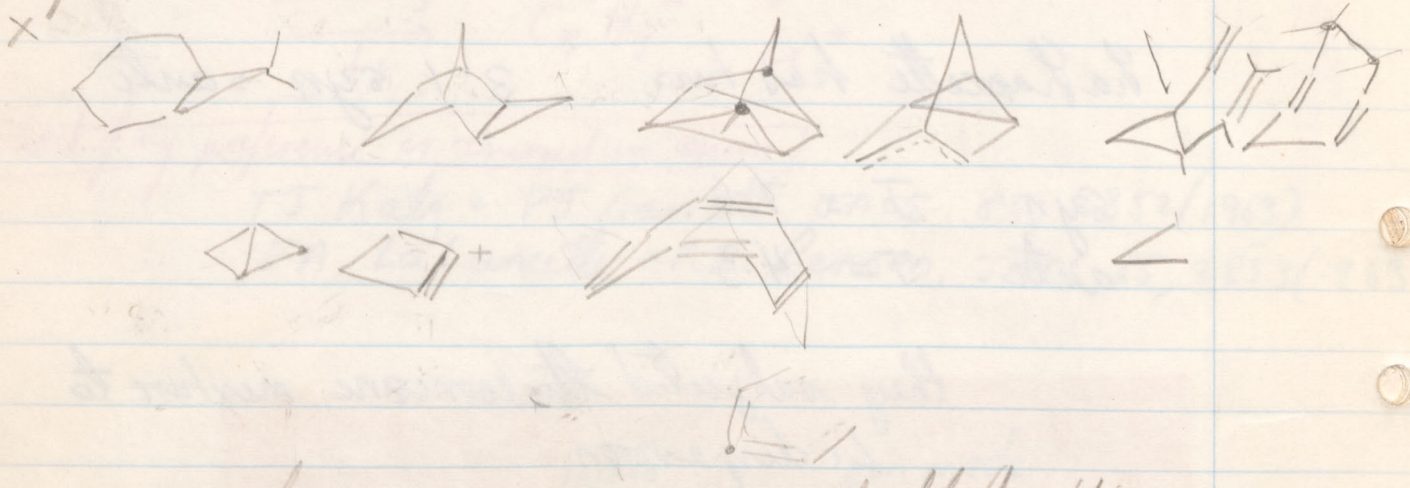
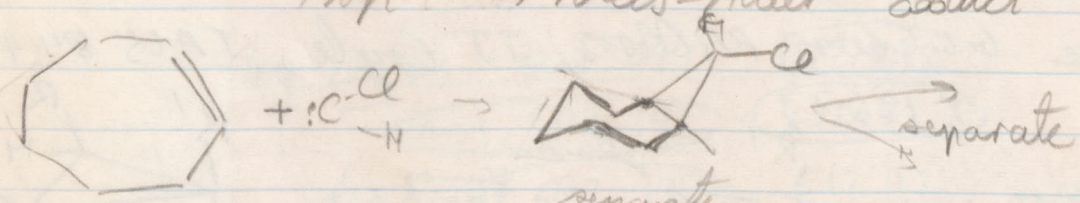
116







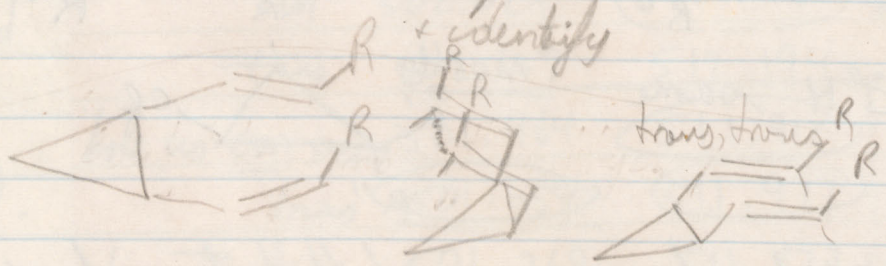
in a large enough ring you might fit the H's on
What is smallest ring with a trans diene. 8.
Top as Diels-Alder adduct

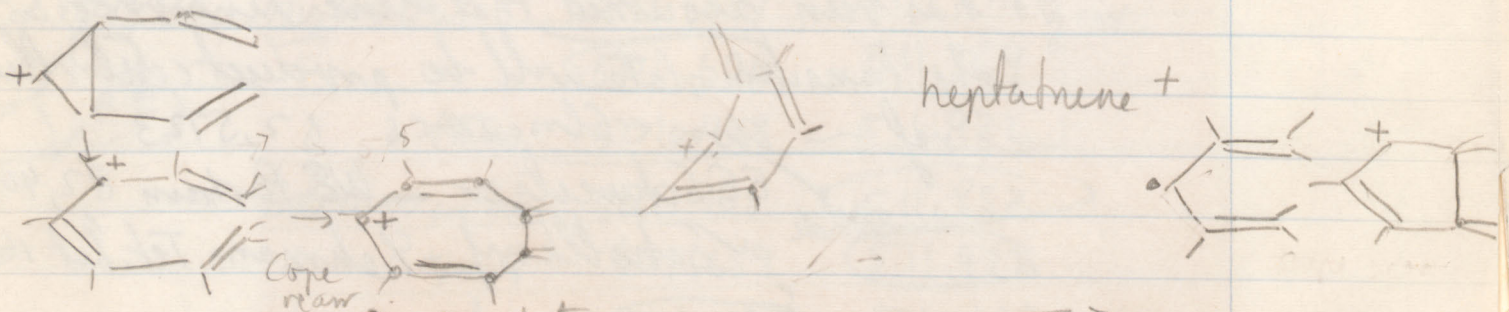


separate
separate
isomers
+ identify

ROH

trans
+ cis cyclooctenone
adducts





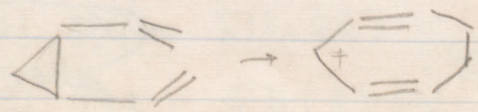
heptatriene +

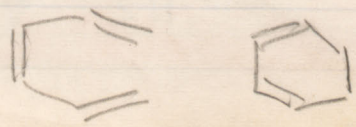
Cope rearr

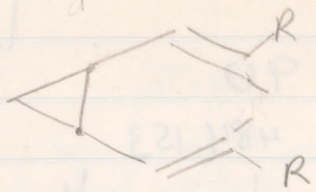
here } disrotatory

III electrocyclic reaction

all electrocyclic reactions are Cope rearrangements

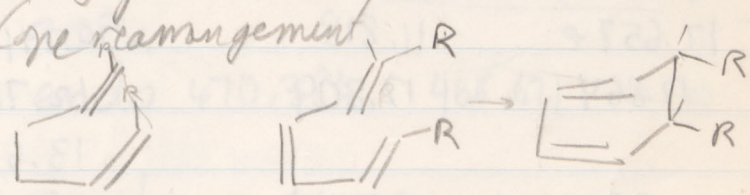


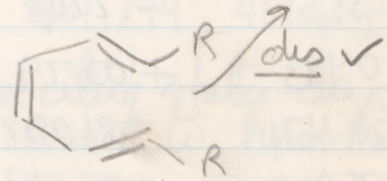


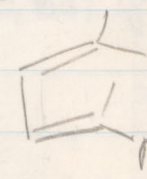


But not all Cope rearrangements are electrocyclic reactions

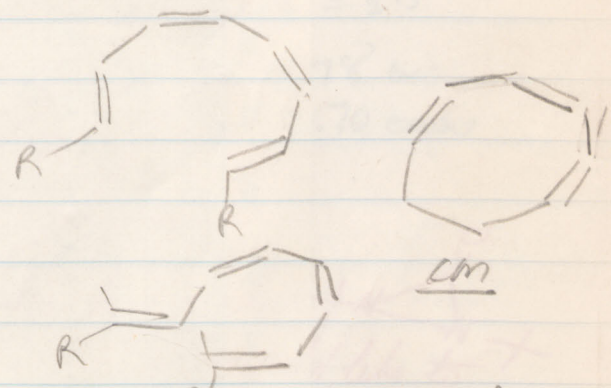
Geometry of transition state matters for Cope rearrangement







hard to Draw Cope rearr. intern

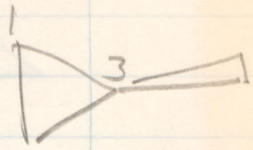


con

Cope dos

we say con

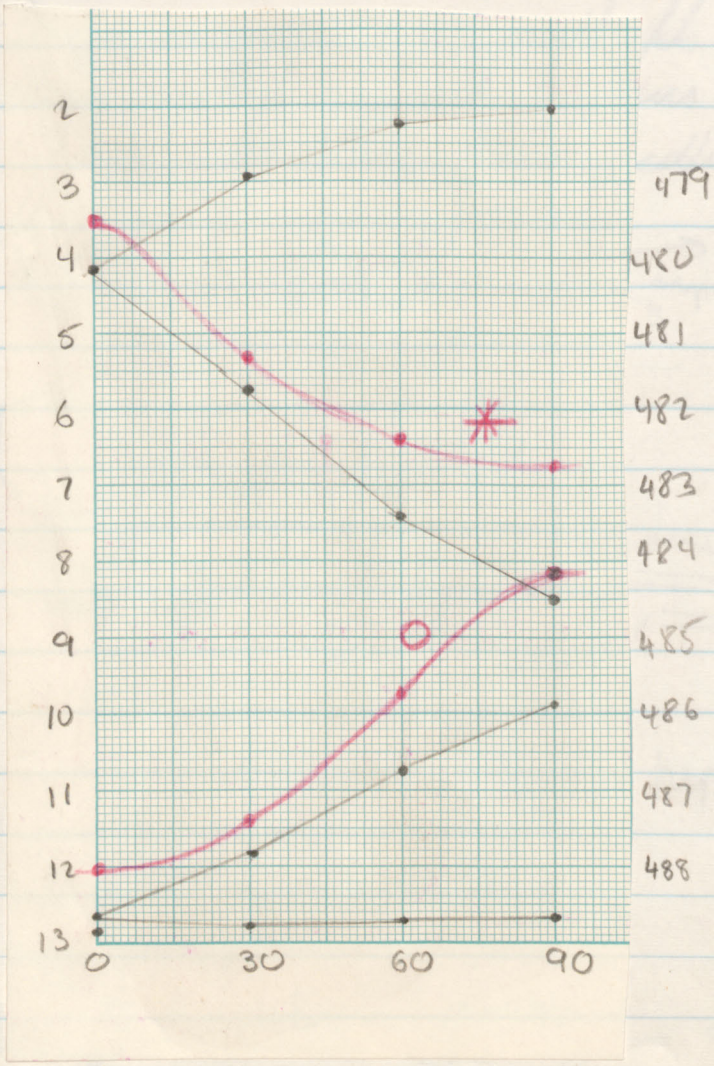
Spiropentane notalms

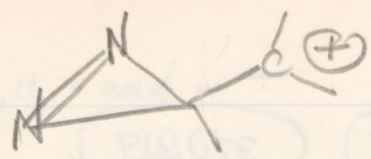


	0	30	60	90
	487.986	487,389	485.750	484,153
		2,919	2,245	2.055
	-4,142 e	5,737	7.393	8.473
	12.657 e	11.818	10,741	9.874
	12.864	12,809	12,716	12,676
			13.60	
C_1	-.2353	-.2243	-,1718	-,0251
C_3	+.0493	+.0079	-.1746	-.7136
*	479.471	481.308	482,402	482.752
+	475.329	475.571	475,009	474.279

~ so partially twisted

— twisted





O 90°

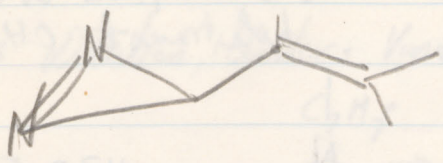
370.598 370.226 Δ = .367

11.035 .384 Δ

13.140 .330

.673

*



exo 470.475 468.724

90°

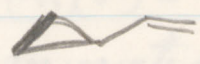
endo 470.384 468.621

exo torsion 467.794 467.614

here excited state doesn't want to twist around double bond; because it's really a π C=C → N=N π* transition

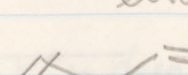
excited states do not want to twist here

Δ = 2.681 ground



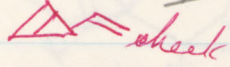
2.89

ethylene = 3.5

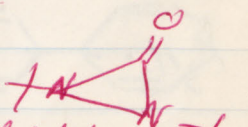


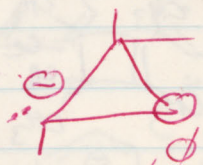
2.78 exo

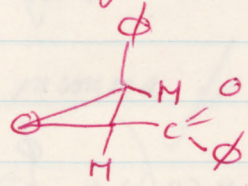
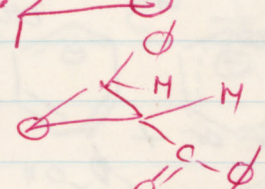
2.70 endo

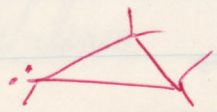
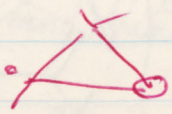
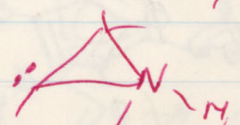
is the same true in  check

---

Deyrup: Fred Greene has made  + would like to know conform.

interested in stability of anions 

thus  +  do not isomerize in pyridine

compare  and  and 

conformational problem here (it's like diazirine)

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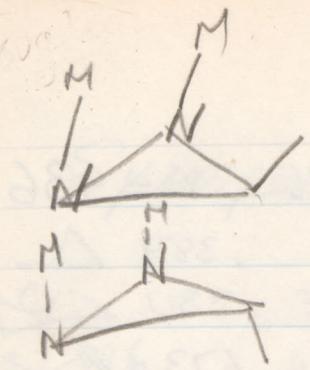
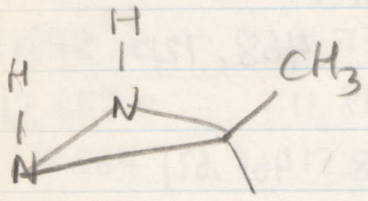


\+ 298,341 | • 309,635 | − 320.919 | 11.294

298,560 | 309,638 | 320.716 | 11.078

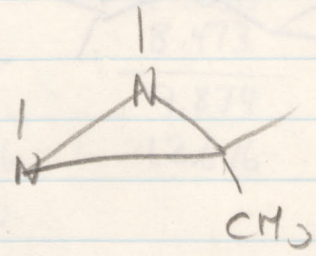
i.e. hole trans to lone pair is better in cation
hole trans to CH_3 was better before

should try trans.

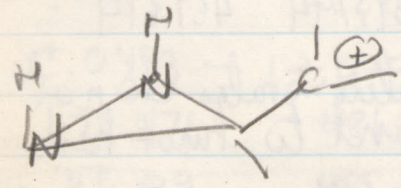


433.526

very little dif



433.539

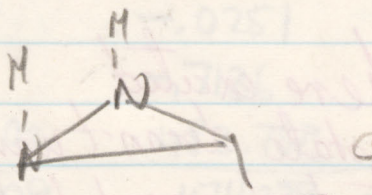


stabilized

0 404.784

90 464.328

.456



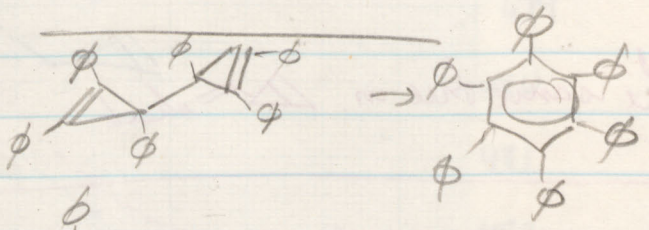
0 404.562

90 404.334

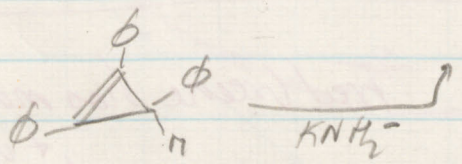
.228

why this dif.?

Brebow



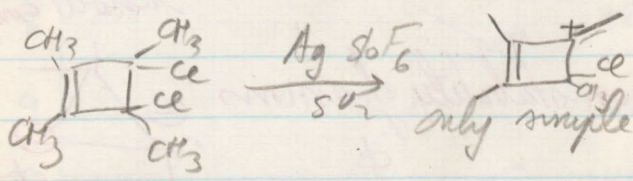
C_3H_3 • or −



KNH_2^-

C_4H_4 + 2

Katz

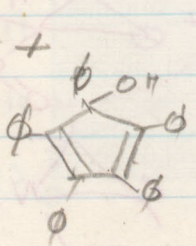


$AgSbF_6$ / SO_2

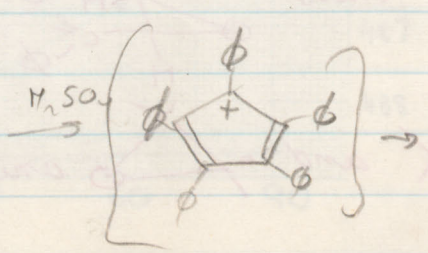
only simple cation is formed

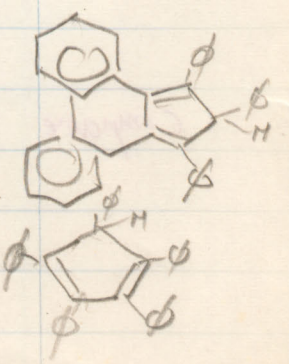
C_5H_3 • or +

Brebow



H_2SO_4





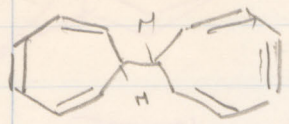
Dauben-Lossing

IP = 8.69 ev

very high for radical

only CH_3• higher

$C_7H_7\cdot$ and —



→ radical → cation

IP = 6.60 eV.
lower than any R·

Dauben, Henderson, Ninan

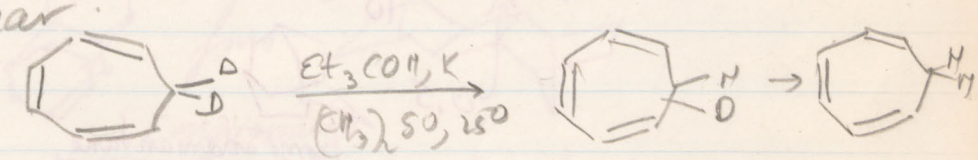
$C_7H_7^+$ 8 evenly-spaced esr lines
⇒ planar, sym.

$D(C_7H_7-C_7H_7) = 29 \pm 1$ kcal.

RE_{emp} (excess over CHT) $(C_7H_7^+) = 23 \pm 1$ kcal.

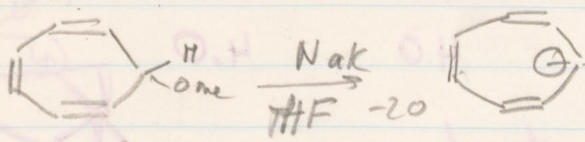
$RE_{total}(C_7H_7^+) = 32$ kcal.

Doering + Gaspar

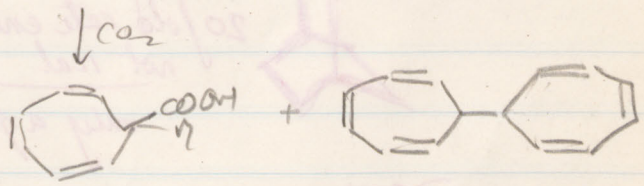


⇒ some anti-aromatic character.

Dauben +

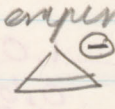
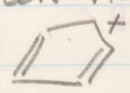
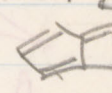
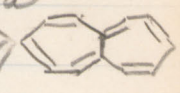


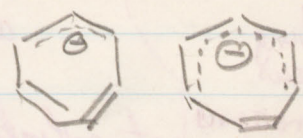
deep blue
no nmr or esr.



estimate empirical excess RE = 22 — 27 kcal.

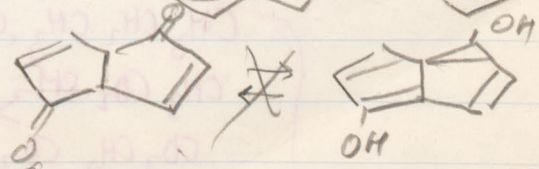
L.C. Snyder

						
$E_{unsym} - E_{sym}$	7.3	11.4	5.2	4.2	0.09	0.3

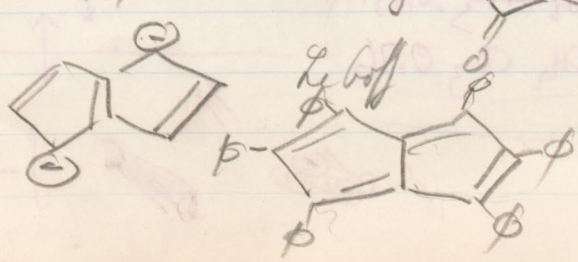
2 mmma fr 

Pentalenes. Brand, Lunstead

Dauben, Ben + Chiang

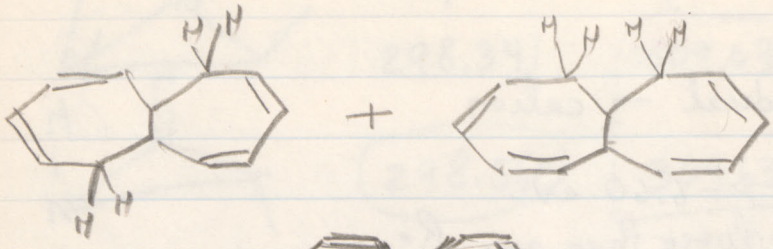


Katz.



Nov. 13

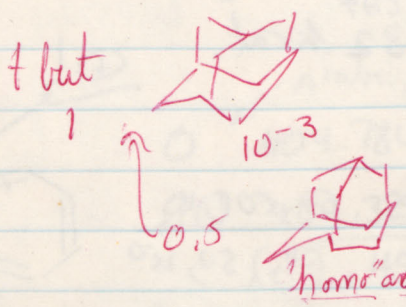
Heptalene

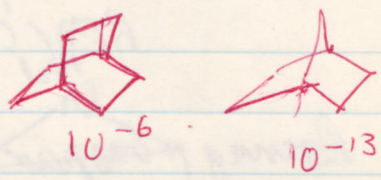


dark brown liquid
O_2 sensitive
unstable >60°

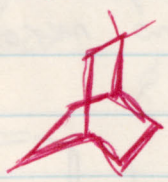
no ring current.

R. Fort: Adamantane.

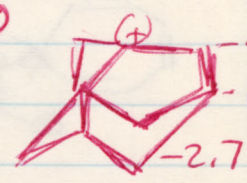


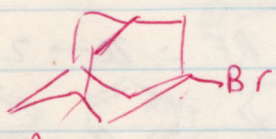


Ground state strain	0	10 kcal	0.0	9 kcal	large
Transition state	0	~10	~4.0	~13.0	very large
Δ Strain	0	0	4.0	4.0	



20 fold rate enh.
not real
only a factor of 2





A

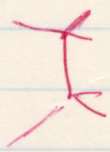
R = H	1.0
me	0.69
Et	1.0
iPr	1.4
also di	0.47
+ trime	0.31

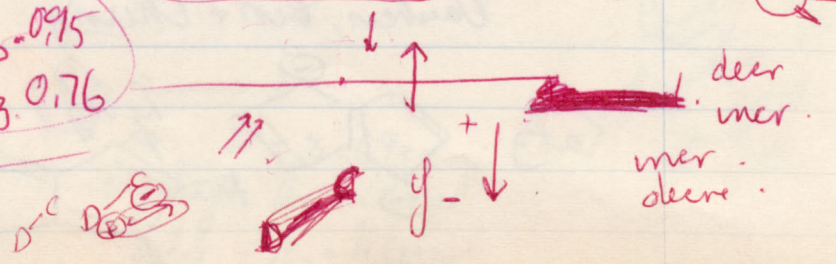
!

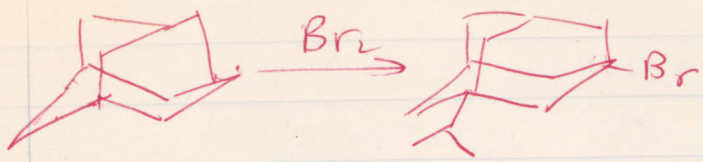
in (adam)⁻ splitting decreases with increasing (Me) substitution. not solvation effects

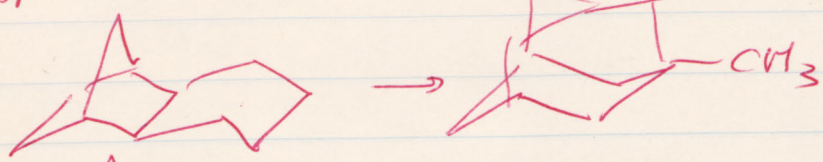
$CH_3CH_2CH_3$	.085
$CH_3CD_2CH_3$	.095
$CD_3CH_2CD_3$	0.76

CH_3 is electron withdrawing wrt H; otherwise inductive order maintained.

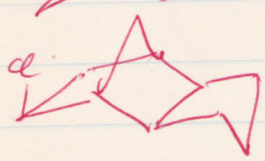




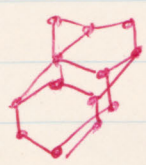




mechanism.



→ adamantane



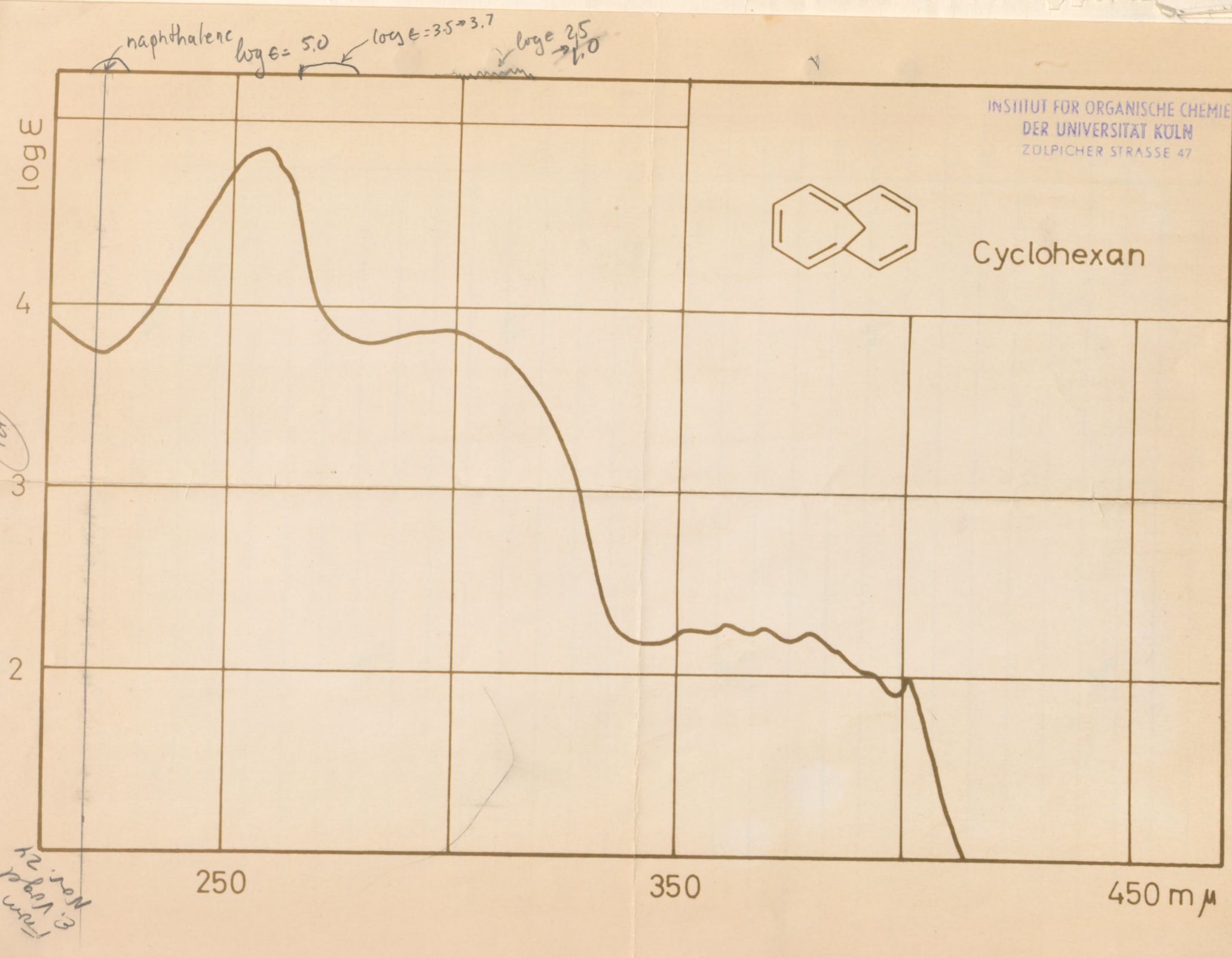
from

congressane.

expect this to be very different.

Brominates to unknown product

(2 possibl.)



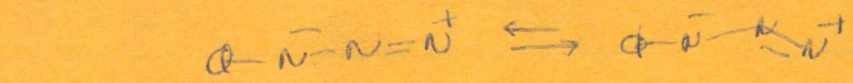
INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
ZÜLPICHER STRASSE 47

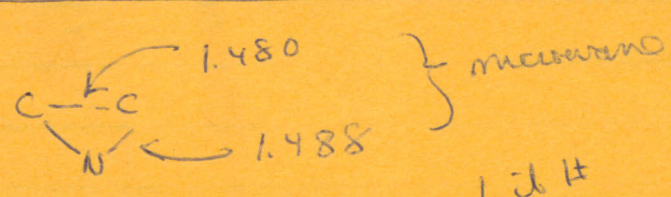
Cyclohexan

Doering

From Doering.

J. D. Roberts ← calculate
Chem. Ber. 94 273

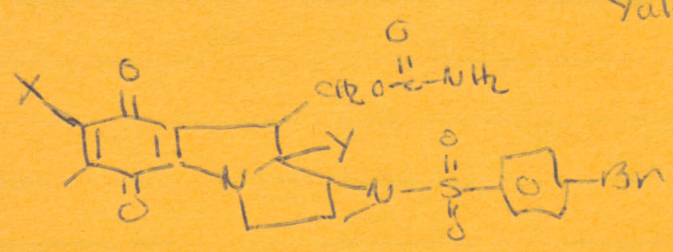




Lit. H

1 H 274
vol 19 p 527
Heterocyclic Compounds

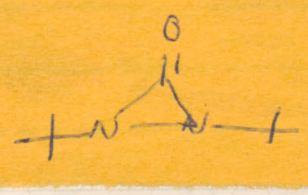
JACS 84 3188 (1962)
A. Tulinsky
Yale



X = O-CH3
Y = O-CH3

structure via X-Ray
but full paper not
out

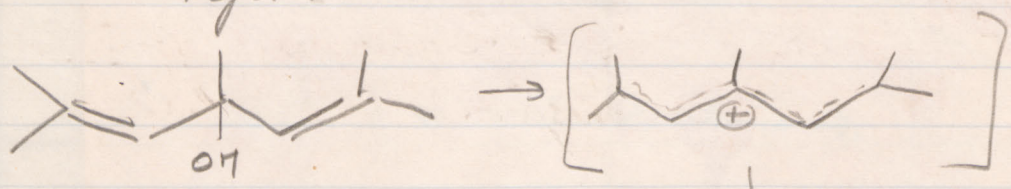
JACS 84 3569 (196X) Greene



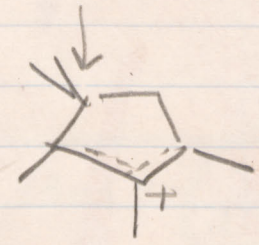
✓

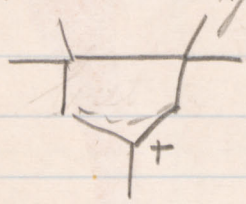
NC Deno + CU Pittman, Jr JACS 86, 1871 (1964)

report

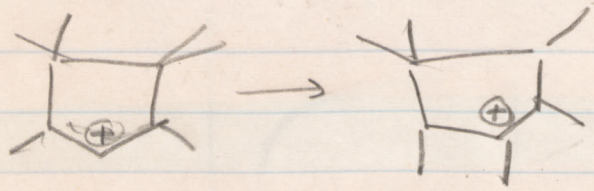


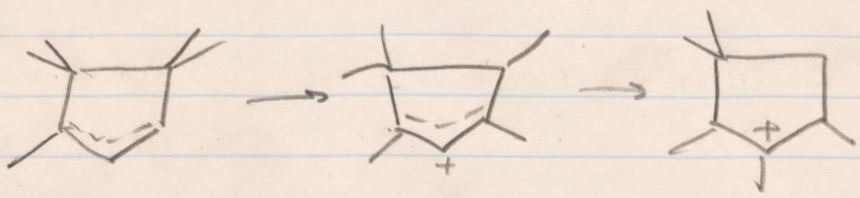
strange; would have expected





but in Deno et JACS 85, 2995 (1963)

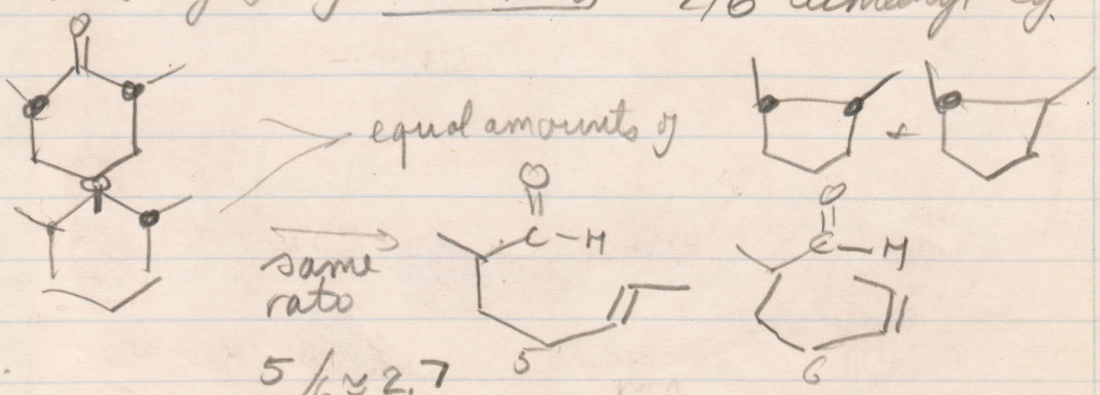




addendum I

B. Ruckborn, RL Alumbaugh + GO Pritchard
Santa Barbara
C + I (1964) 1951

Photolysis of <u>as + trans</u> 2,6 dimethyl cyclohexanone



see ref.

thus apparently concerted mechanism is unlikely

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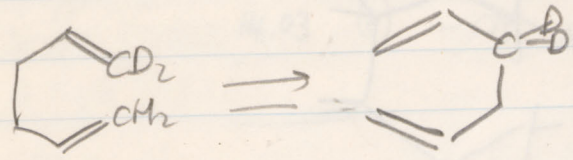
Doering:

$CH_3-CH_2CH_3 \rightarrow CH_3\cdot + \cdot CH_2CH_3$ 82.5 kcal

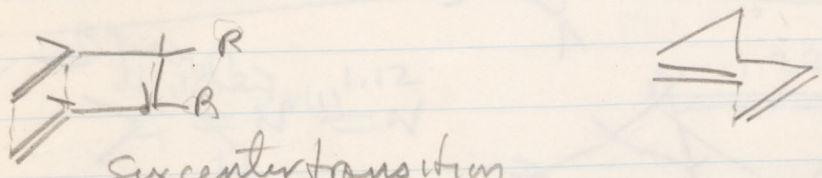
$CH_3-CH_2CH=CH_2 \rightarrow CH_3 + \cdot CH_2CH=CH_2$ 62.5

allyl stability ~20



E_a = 34.5 kcal

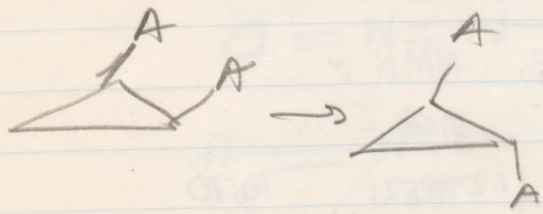
$\Delta S = -11$



4 center

Six center transition state; RBW thinks its stereo course.

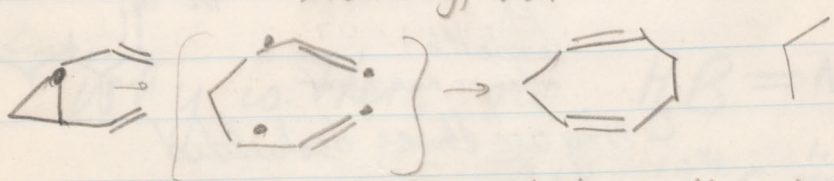
5-6 kcal seems too large for simple ground state eclipsing.



E_a = 64.2 kcal A=D Strain = 27.6.

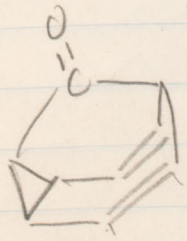
59.4 A=Me Assistance ~18

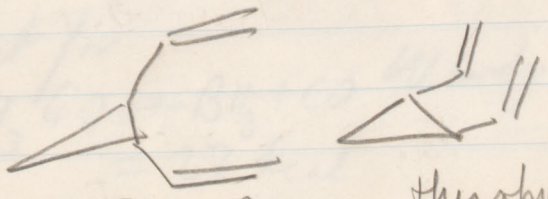
One gets a large piece of strain showing, but not all.



stability = strain relief + 2 allyl del ~ 3×18 = 54.

83 − 54 = 29 ≈ E_a observed.



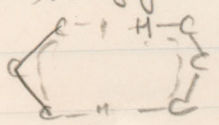


12 for cope

−6 for 6 center

this should be at most 6 kcal less but it goes down too much → about 10

"benzylic" resonance

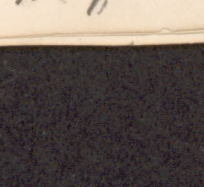


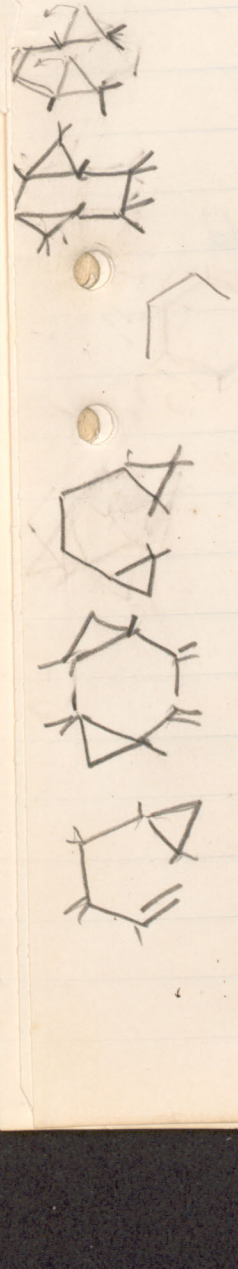
in plane

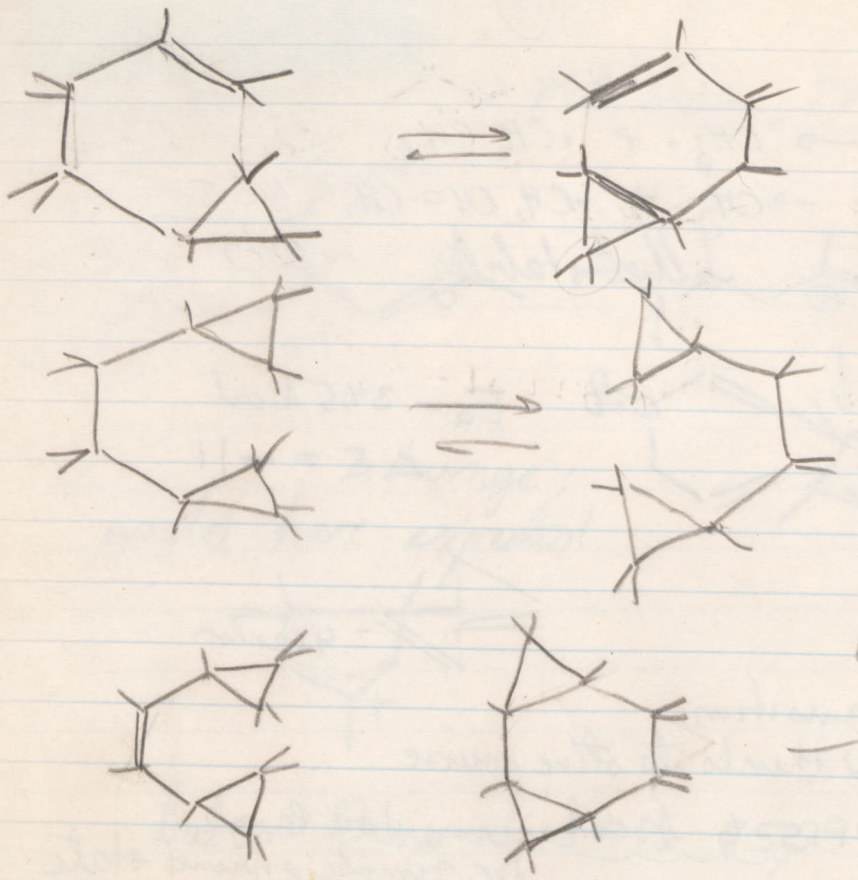
in tricyclic compounds these can be brought closer together

unexpected help of 10−14 kcal

E_a ≈ 28

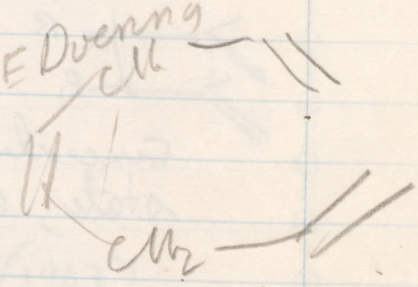






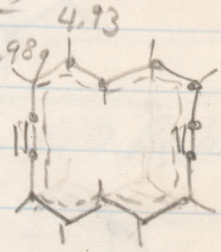
MBF_2

W v E Doering



Bartlett

Ring size	No. of ≡	NMR τ	
12	2	5.58	
14	1	1.2→2.7	10.70
14	2	1.57 (d, J=8.0)(4)	15.54 (t, J=18.3)
		0.45 (d.d, J=8.0, 13.3)(4)	
16	2	2.25	4.35 4.93
18	3	1.90 q	2.44 q. 2.98 q 8.26 dd
24	4	1.80 dd	3.67 4.2



inside H's when no ring current

why are these deshielded

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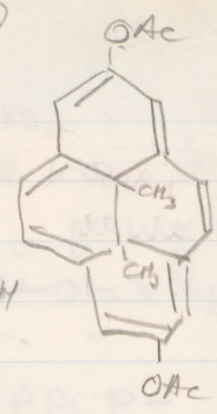
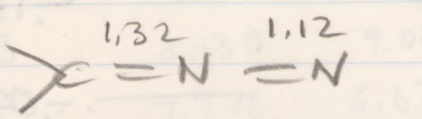
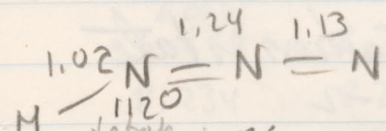
Bockelheide

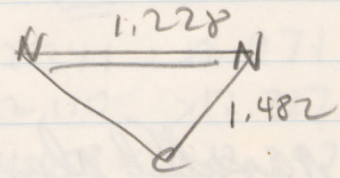


C14

NMR 1.42 (4) } perigh. H
1.36 (4) }
7.50 (6) -OAc
14.03 (6) $-CH_3$ very shielded

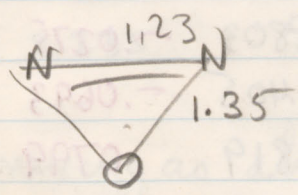


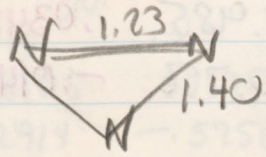




∴ in cyclic forms of HN_3 ↓ $+ N_2O$

assume N=N as in diazirine = 1.23 and take X—N 0.16Å longer than in linear compounds





Why do there no $H_3B{=}N{=}N$

$BH_3 \overset{1.54}{=} C \overset{1.13}{=} O$

Bauer 1937
JACS 59, 1804.

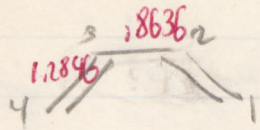
East / nr
$BH_3CO \rightarrow BH_3 + CO$ W. Gordy PR 78, 1482 (1951)
$= 27$ kcal

$BH_3 + BH_3CO \rightarrow B_2H_6 + CO$

Nov. 13

Diels-Alder 130

$\gamma_H = 1.3$



far away, i.e at ∞

C=C C=C−C=C

16 −8.238

17 −9.199

18 −12.473

19 −13.218

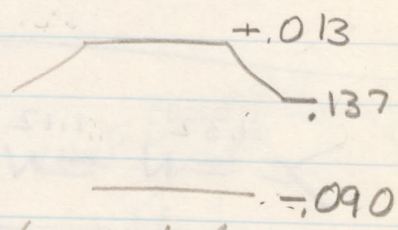
$\Sigma = 601.764$

$-.8276(z_5+z_6)$

$.6422[z_1+z_4] - .4651[z_2+z_3]$

$-.5305[z_1-z_4] - .3663(z_2-z_3)$

$.6275(z_5+z_6)$



Now parallel plane transition state

		at −3 below	1-5 n	at −2	
−3	center	601.758	0.0000	601.659	.0000
−2		601.730	−.0001	600.953	−.0022
−1		601.641	−.0012	598.803	−.0275
0		601.536	−.0016	596.405	−.0693
1	1-5 = 3.09 Å	601.569	.0038	596.819	.0799
2		601.661	.0026	598.985	.0345
3		601.726	−.0002	600.756	−.0147

−3	−3	−8.238	−9.198	−12.473	−13.217

16 mixes in $.0045(1-4) - .0045(2-3)$

17 $.0029(5+6)$ + ∪ orb.

18 $-.0010(5-6)$

19 $.0082(1+4) + .0074(2+3)$

−3	−2	−8.237	−9.195	−12.471	−13.203

same pattern.

−1	−8.247	−9.180	−12.467	−13.129
0	−8.219	−9.180	−12.473	−12.999
1.0	8.166	−9.186	−12.479	13.035
2.0	8.216	−9.178	12.466	−13.156

π π*
+ =
orbitals!

So ethylene π mixes in lowest diene state
π* " " " highest
diene π mixes in ethylene π*
π* " " " π

at 1.0, 0, 0 there's a switch ← + ethylene π* mixes in diene π, others same
at 2.0 switch back

		═	═╲	╱═	═
at 2.0	+3	8.130	9.088	12.341	12.971
	+2	7.776	8.672	12.110	12.387
	+1	~~6.528~~ 6.062	8.748	11.058	12.397
	0	8.234	8.283	10.836	12.278
	−1	8.325	8.716	12.115	12.385
	−2	8.182	9.136	12.432	13.030
	−3	8.235	9.196	12.472	13.207

+3 mixing as above
−2 " 16 " 17 " 18 19
−1 −.3105 .5713 .3638 .5452
+.2914 −.5258 .1692 .3384
−.2914 −.5258 .1692 −.3384
−.3105 .5713 .3638 −.5452
−.6961 −.2039 .5150 −.0981
.6961 −.2039 .5150 +.0981

0 −.4928 .4727 .5109 .4731
+.3052 −.5697 .1453 .3678
−.3052 −.5697 .1453 −.3678
+.4928 .4727 .5109 .4731
−.5735 −.3146 .4615 −.2343
+.5735 −.3146 .4615 .2343

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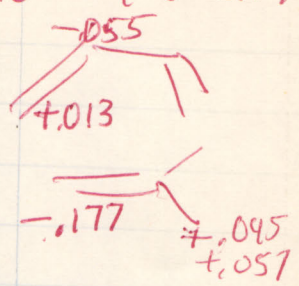
1

6.527	1.062			
∓.0555	−.5530	∓.6788	.1196	±.5064
−.4475	+.6190	.3893	.4398	±.3244
.4475	−.6190	.3893	.4398	∓.3244
±.0555	+.5530	−.6788	.1196	−.5064
∓.7423	−.3231	−.1541	.5248	−.2458
+.7423	.3231	−.1541	.5248	.2458

at 1.0 1-5 = 2.149



so ethylene is acceptor

sw. sign

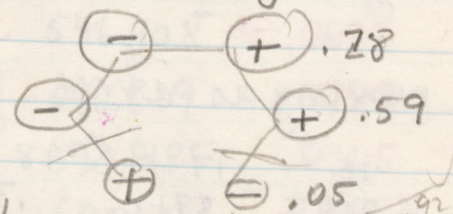
2

+.0931	−.6721	+.5161	.0274
−.4355	+.3992	+.3540	.3358
+.4355	+.3992	−.3543	.3358
−.0931	−.6721	−.5161	.0274
∓.7051	−.1826	−.1575	.5415
+.7051	−.1826	.1575	.5415

π_4
π_3
π_2
π_1

ethylene π mixes in butadiene π_1
diene π_2 mixes in ethylene π^*_x

highest MO = "π_2"

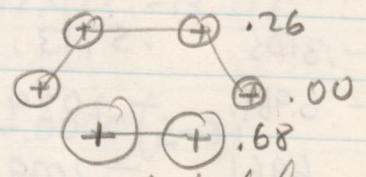


9 at +2

it doesn't move much since it has nodes.

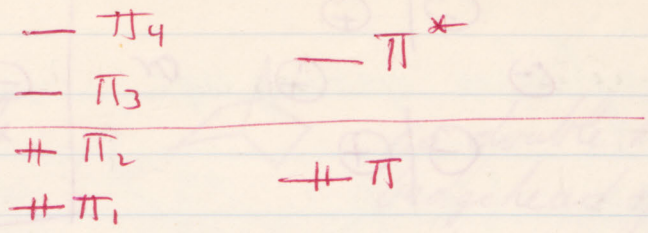
on the other hand

π =



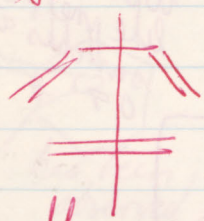
is very destabilized + becomes highest occupied near t.s.

Note that as we get close to product this must happen, since we must get a 2-3 π orbital (see at +1)



Butadiene ethylene

In transition state which preserves central plane of symmetry



the following will mix (π, π_1, π_3) ; (π^*, π_2, π_4)

thus new "π" = $a\pi + b\pi_1 + c\pi_3$ $\quad a > b, c$

Now the mixing is greater the closer in energy the orbitals are : $\therefore \; b > c$

"π" = $a\pi + b\pi_1$ denoted as $\pi + \pi_1$

"π_1" = $\pi_1 + \pi + \pi_3$

"π_2" = $\pi_2 + \pi^* + \pi_4$

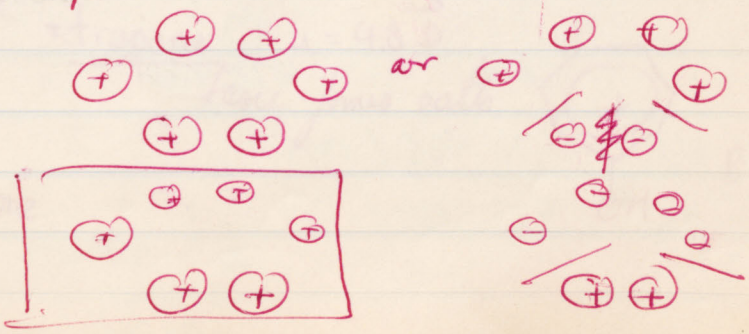
"π_3" = $\pi_3 + \pi + \pi_1$

"π_4" = $\pi_4 + \pi^* + \pi_2$

"π^*" = $\pi^* + \pi_4 + \pi_2$

for occupied levels we're only concerned with "π", "π_1", "π_2" + only antibonding that is mixed in is π^* in "π_2" (also π_3 in "π" but that is small) so that net effect is charge transfer butadiene → ethylene, which does indeed show up.

Now "π_4" can be



"π" mixing only π_1

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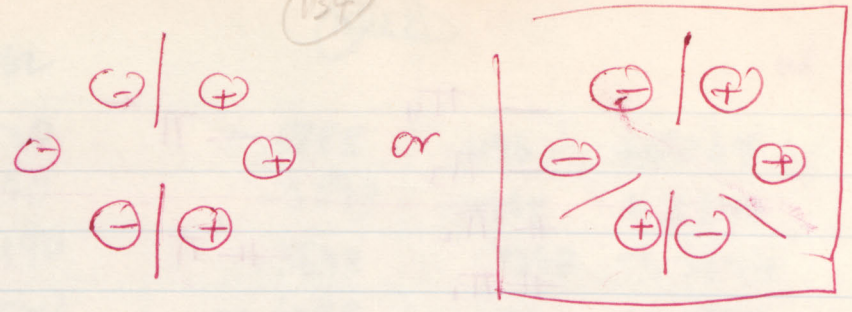
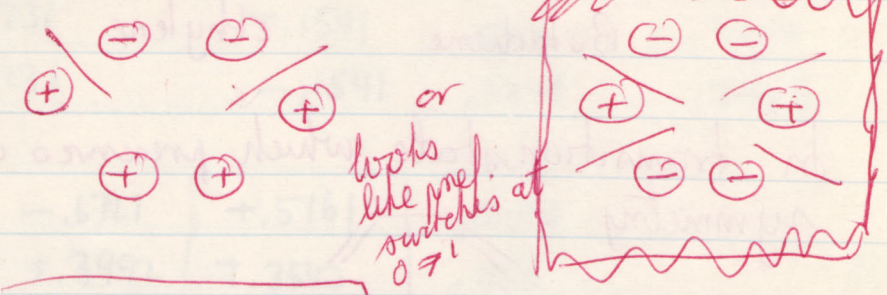
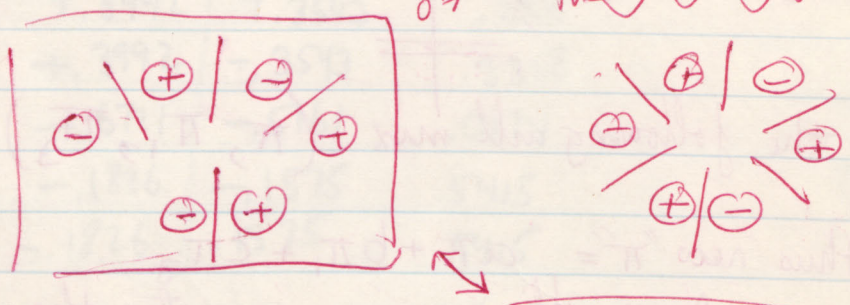
π_2



π_3

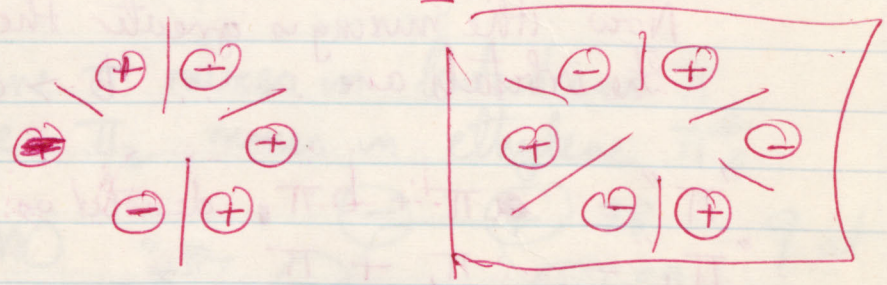


π_4



π^*

mixing only π_4



if two levels interact the higher energy one takes the ~~be~~ more bonding combination

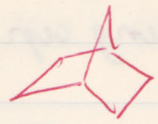
✓ $\underline{\pi_4}, \underline{\pi^*}$

π_3, π

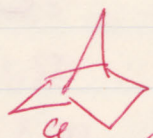
✓ $\underline{A_2}\ \pi_x$

✓ $\underline{\pi}\ \pi_1$

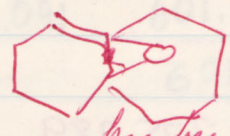
Bartlett.

Bredt's rule:  no double bond at bridgehead of such a system.

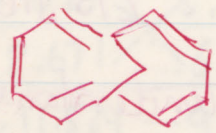
must be relaxed.



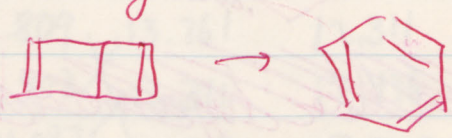
Ce $+ SbF_5 + SO_2$ gives carbonium ion.



has been observed

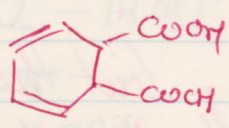
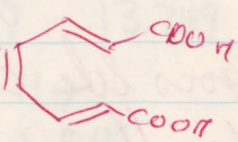
What gives  from

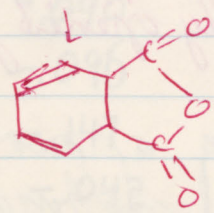
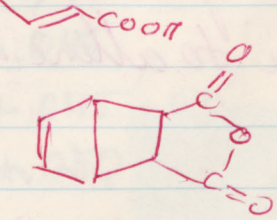
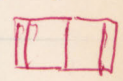
and keeps "Dewar benzene" intact



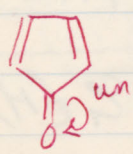
is the electrocyclic reaction exothermic over 50 k cal.

(has

he tried  

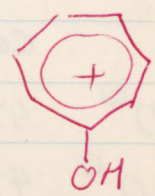
$Pb(OAc)_4$ diacid

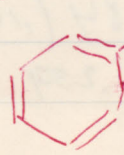


unhappy since O electron withdrawing

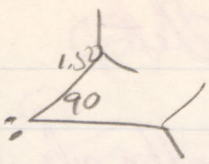
should be therefore very happy.

=tropone $\mu = 4.3\ D$

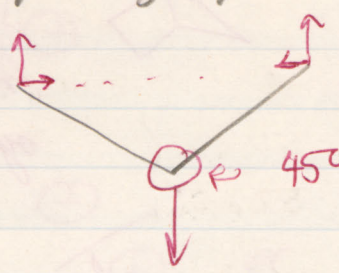
taste forms salts  Br^-

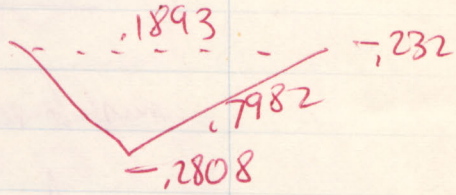
 tropolone

Cyclopropylidene opening up

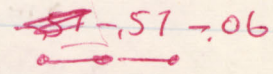


8 −10.033
9 −10.522

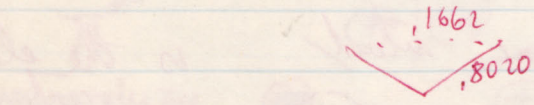




	con	dis
	275,160	
10°	275.072	275,289
20°	274.814	275,476



I don't understand this.



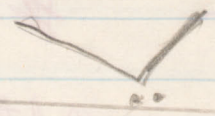
~~It goes like hydroboration~~

It goes like cation, but that just can't get you to allene in fully opened form

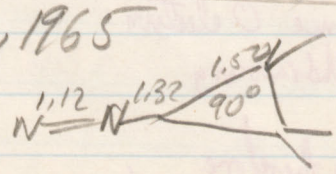
1998, July 4

This date (3/17/65) is strange

In one sense a carbene is like a carbonium ion

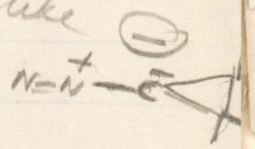


March 19, 1965



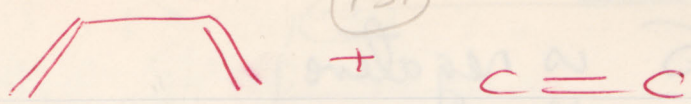
$\varepsilon(H) = 1.3$

so this reacts like



	con	dis.
	472.426 (.1846)	
10°	472.408 (.1709)	472.384 (.1805)
20°	472.360 (.1316	472.259

* 470.812
470.802 470.851
470.765 470.946



c = c at 1.25, ±.67, x

	x	$c_1 - c_5$	E	n(1-5)	x-M	$S(P_{z_1} - P_{z_5})$
1	-1.00	1.247	562.678	.3474	1.14, 1.43, 1.33	-.084
2	-1.25	1.456	577.261	.3886	1.37, 1.53, 1.64	-.187
3	-1.50	1.675	586.974	.3478	1.60, 1.74, 1.84	-.220
4	-2.00	2.135	597.483	.1015		-.173
5	-3.00	3.091	601.595	.0046		-.044
	∞		601.764	0		0

			∞	-3	-2	-1.5	-1.25
a	π_y	15	6.346	6.346	5.800	2.044	+1.513
a	π^*	16	8.238	8.177	7.029	5.690	-1.122
s	π_3	17	9.199	9.182	8.671	6.197	5.727
a	π_2	18	12.473	12.476	11.524	9.538	8.573
s	π	19	13.218	13.069	12.328	11.459	-10.389
s	σ	20		13.807	13.809	13.261	12.311
a	σ	21		14.044	13.902	13.311	12.496
s	π_1	22		14.052	14.087	13.817	13.749

Q	1	2	5	H_7
∞	-.137	+.013	-.090	+.045
-3	-.129	+.010	-.096	+.045, +.045
-2	.000	-.079	-.147	+.050, +.053
-1.5	-.104	-.207	-.042	
-1.25	-.271	-.123	-.117	
-1.0	-.421	-.119	-.216	

H_5 ⊕

funny charge behavior

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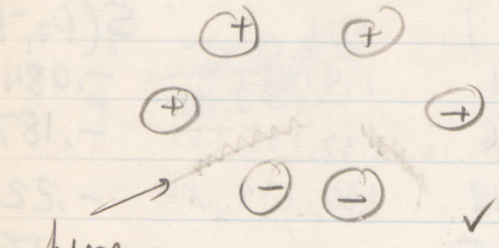
S is negative

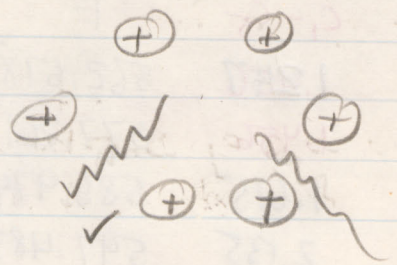
π_1 also some π_3

∴



here ⊕ ⊖ no node

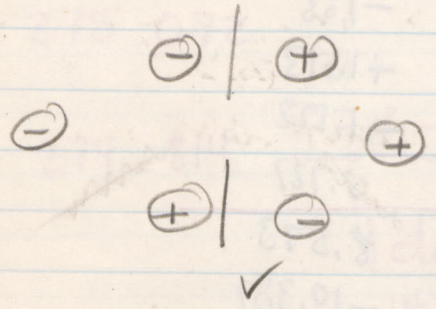
π also some π_3



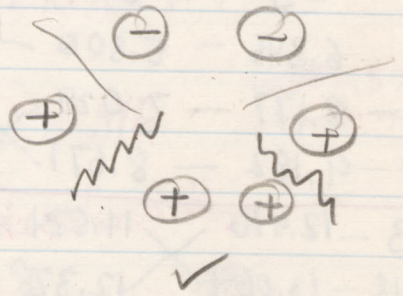
again cancelling at −2

.0695
.4007
−.4507
.0695
.5027
.5027

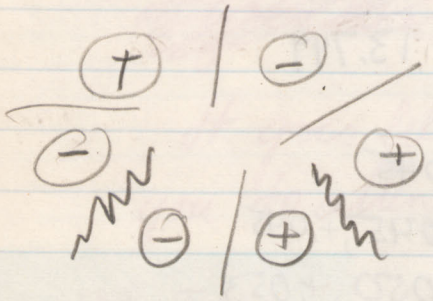
π_2 also some π_4



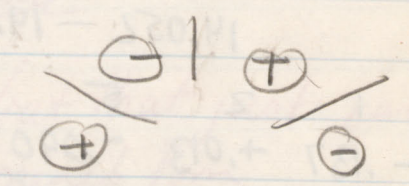
π_3 also some π_1



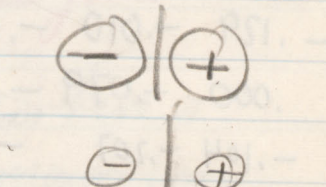
π_4 also some π_2



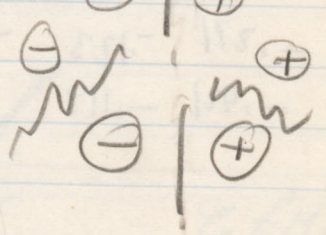
π^* also



at −2



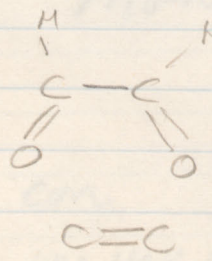
at −3



mixture at −2

.0775
−.5666
.5666
−.0775
−.6366
.6366

Things would be different if transitions to state twice in plane then S = +



C=C

correlation diagram

now we are concerned with

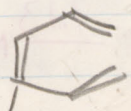
$\pi_1, \pi_2 + \pi$

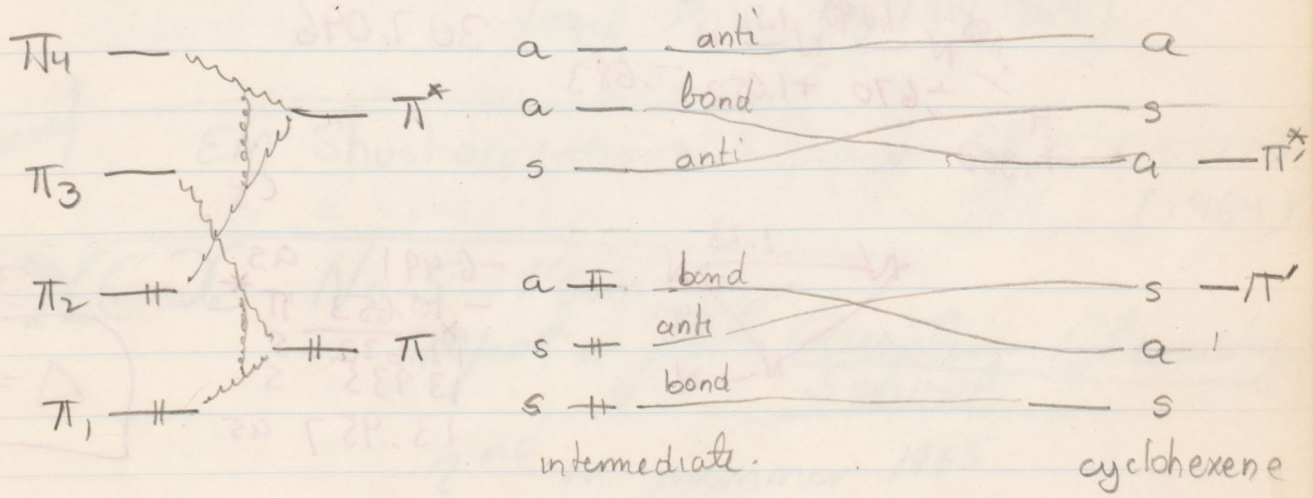
main mixing of antibonding orbitals is π^* into π_2 $\Rightarrow$ diene → olefin charge transfer.

$\pi_1 + \pi_2$ are bonding in new bond region + will not change drastically in energy with approach. π is antibonding + will be destabilized. New 2-3 bond must come from (π); π is highest filled and is <u>destabilized</u>

at -2 ≈ 12.6% CT to olefin

2,3 antibond must come from <u>π_4 or π_2</u>

this is not quite like  since orbitals must have an <u>even number of nodes</u>



Nov. 13

1.126 1.186
N ═ N ═ O
1.5613 .9353
−.537 + 1.320 −.762

N ═ N
1.13
1.35
O
↓ y
z
319.338

eπ −8.740 x.y
eπ −14.106 xy
−15.159

.7215 −.8792 +.4225
.6509 N₁ + .2158 N₂ = .73290

−7.294 b_2
−10,653 π^* a_2 ↑ B_2 allowed } in
−13.040 π b_1
−13.903 a_1
14.929 b_2

313.653

Δ = 5,685

1.0783
+.292
.3768
−.583

hydrazoic acid $\mathcal{Q}_H = 1.3$, ∠ NNH = 120° N−H = 1.0Å

N 1.24 N 1.13 N
1.0 1200
H

−8.448 π
−8.891
−13.264 π
−13.721

abs. 2603 (in H_2O)
Θ = 43
Chisson + Craig

C_s

.685
N 1.090 N 1.511 N
÷.670 +1.052 −.683
H
+.300

307.096

C_s

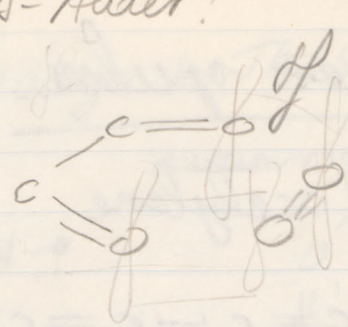
1.23
N
1.40
H

−6.491 as
−10,653 π^*_s
12.630 S
13.935 S
13.957 as

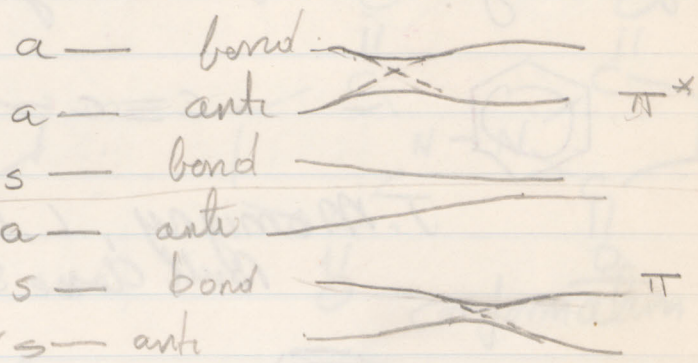
301,971

Δ = 5,125

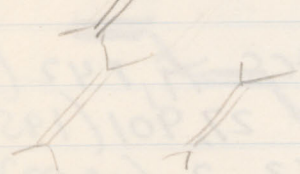
Diels-Alder:



If transition state were in plane,
$S > 0$

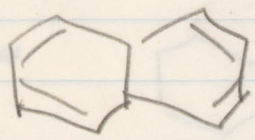


This is not a good way to make a Diels-Alder adduct



Is it a good way to make a 1,2 adduct?
probably not.

On COT inversion -
FAL Anet, AJR Bourn + YS Lun
JACS 86, 3576 (1964)



Vogel AC 76, 786 (1964)

added EM Shustorovich + N.A. Popov JCC X 5, 770 (1964)

JCC X No 5 1964
report on first Quantum Chemistry School
2nd in summer 1965

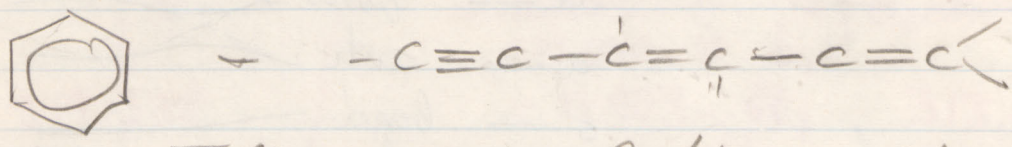
write to Kurt Fahey

Nov 13

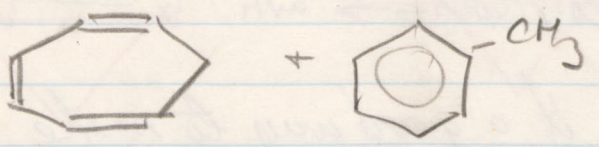
(142)

On commonness in mass spectra

C_6H_6 benzene + butadienyl acetylene

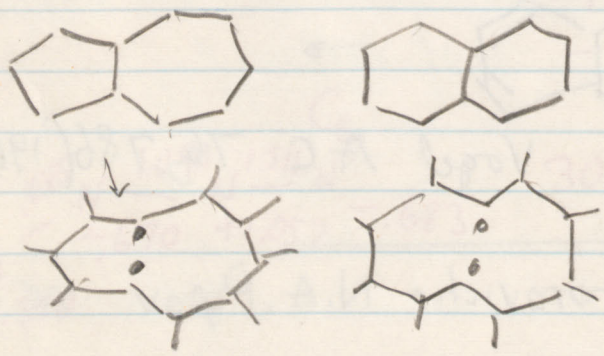


J. Momigny, L. Brakier + L. D'Or.
Bull Classe Sci Acad Roy Belg 48, 1002 (1962)

C_7H_8 

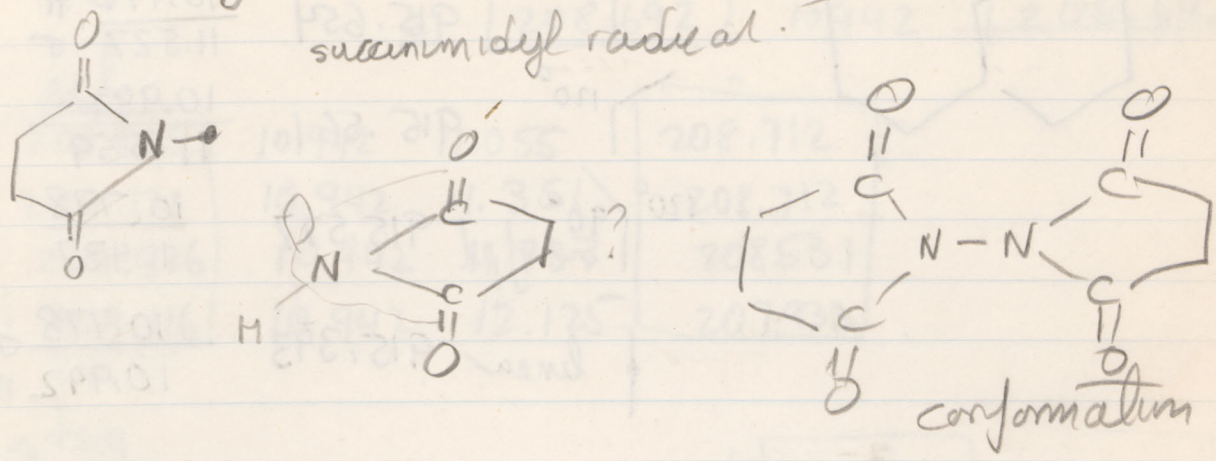
$C_7H_7^+$ Meyerson + Rylander JACS 79, 842 (1957)
JCP 27, 901 (1957)
JPC 62, 2 (1958)
JACS 85, 3340 (1963)

Azulene + naphthalene
RJ Van Brunt + ME Wacks
JCP 41, 3195 (1964)

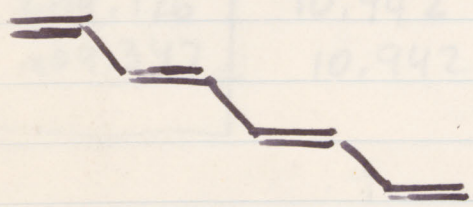


E. Hedaya et al JACS 86, 2727 (1964)

succinimidyl radical.



conformation



$\frac{9.647}{11.965}$ 736.852

8 ✓✓
1,7 → 1,2,5 → 1,2,2,3 → 1,2,2,2,1
→ 1,6,1 → 1,2,4,1
→ 1,4,3 ~~

3,5 → 3,2,3 ~~

9
i.e. ~~10~~ conform. torig = 10

easiest way to to subdivide max = 1,2,2,2,1
+ group all ways

for 6 = 1|2|2|1 1,5 1,2,3 1/2/4/1
3,3 1,4,1
5 partition

4 = 1|2|1 1,3 1,2,1 2

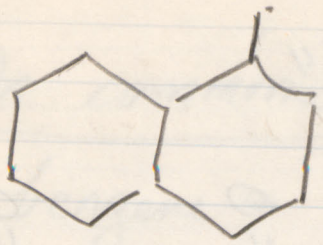
n	part-1	part-2 ℓ
4	~~2~~	1
6	~~3~~	4
8	~~4~~	9
10		16

Nov. 13

Carbenes

144

$C_{11}H_8$



120°

915.654 — 10.992 / 11.527 (π / σ) — 915.119 *

120°

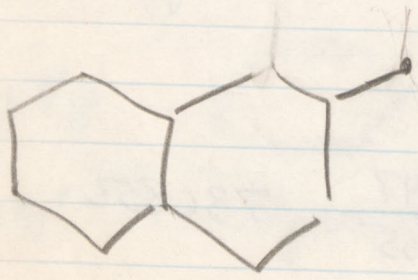
915.561 — 10.992 / 11.559 — 914.995

120° / 90° out of pl

915.577 — 10.778 / 11.437 — 914.918

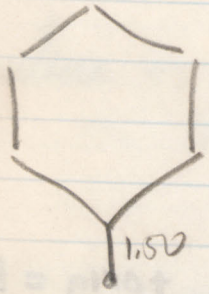
linear

915.393 — 10.778 σ / 10.992 π — 915.289



linear

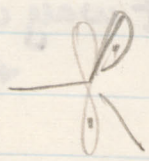
915.345 — 10.814 / 11.011 — 915.148



○	598.349	11.048 / 11.610	597.787
30	598.341	10.999 / 11.602	597.738
60	598.337	10.988 / 11.590	597.635
90	598.340	10.827 / 11.585	597.582

linear

598.092 — 10.827 / 11.048 — 597.871



Ethylidine

180°

e | 208.692 | 10.942 | 208.692

ecl

160	208.825	10.942	11.055	208.712
140	209.121	10.942	11.351	208.712
120	209.326	10.942	11.737	208531
100	209.116	10.942	12.125	207.933

stag

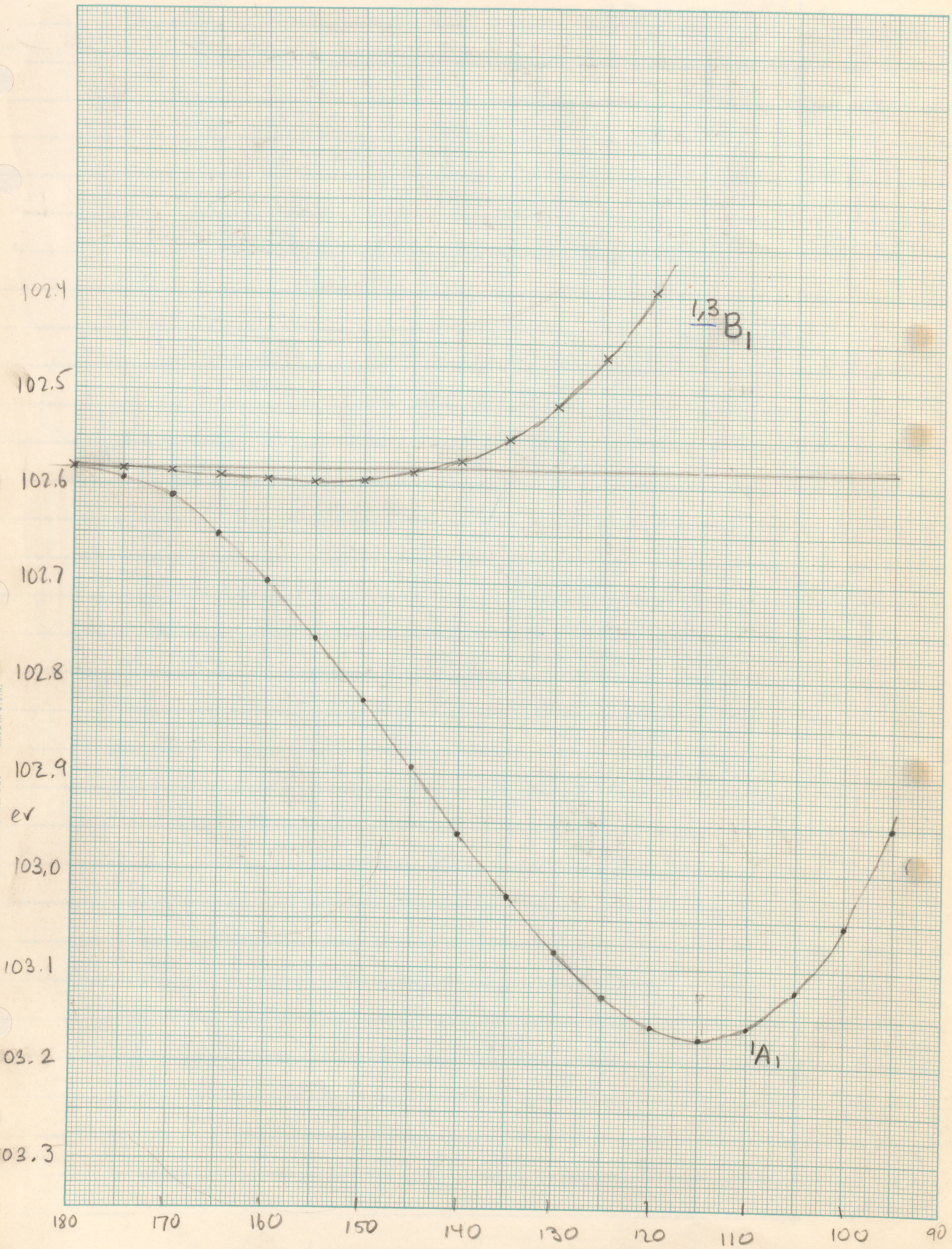
160	208.826	10.942	11.055	208.713
140	209.126	10.942	11.353	208.715
120	209.347	10.942	11.745	208.544
100				

4

Nov. 13

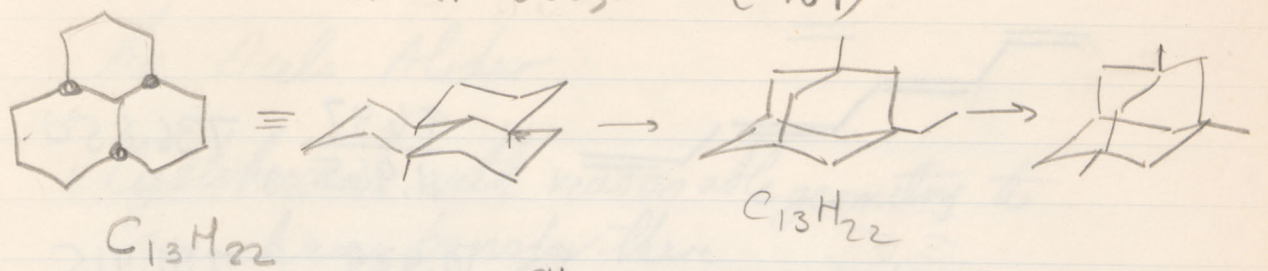
Carbenes

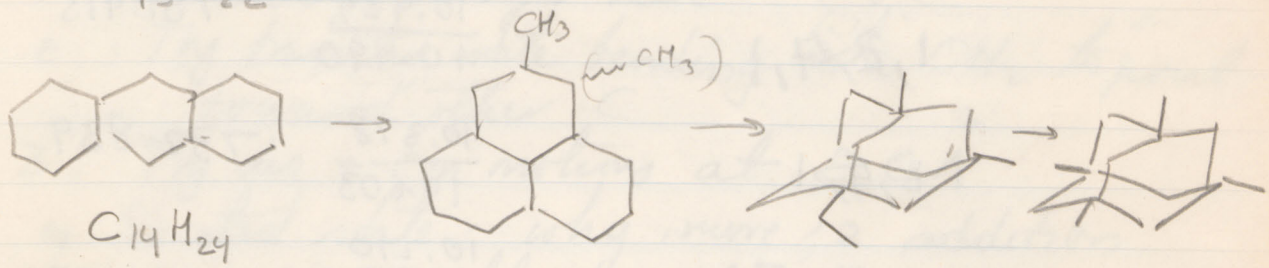
Methylene

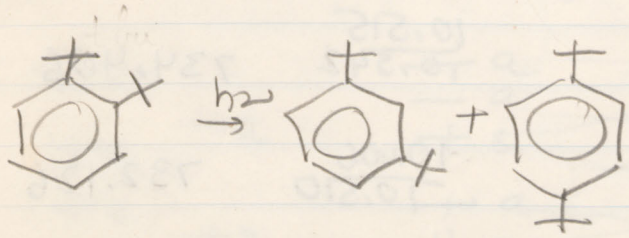


10 X 10 TO THE CM. KEUFFEL & ESSER CO. 358-14B MADE IN U.S.A.

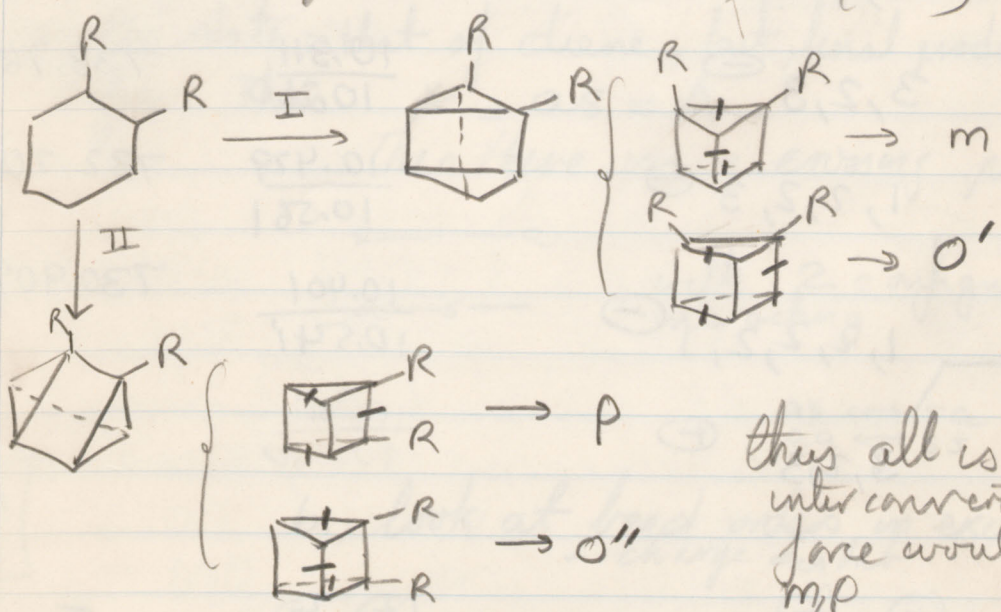
Schneider et al JACS 86, 5365 (1964)





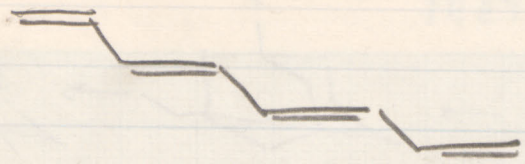


Burgstahler JACS 86, 5281 (1964)

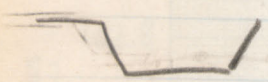


thus all isomers interconverted, driving force would be for m, p

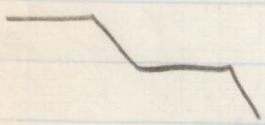
Wilzbach + Kaplan JACS 86, 2307 (1964)



	9.647 / 11,965	736.850	734,532
1,2,4,1	10.439 / 10.490	731.415	731.374
3,4,1	10.378 / 10,603	732.839	732.614
1,2,5	10.270 / 10.774	733.537	
3,5	10.515 / 10.542	734.406	734.379
1,6,1	10.406 / 10.510	732.126	
1,7	10.456 / 10.522	734.101	734.035
3,2,3 ⊖	10.311 / 10.760	733.760	



1,2,2,3 ⊖	10.429 / 10.561	732.202
1,2,3,2,1 ⊖	10.401 / 10.541	730.909
3,2,3 ⊕		

⊕ = 

Re Diels Alder

1. Cyclohexene with reasonable geometry to see charge transfer there
2. Try transition state bending back CH_2 to "point toward" other C
3. Try dis + con motions at 2.0 Å
4. Excited state; why more; 2 additions
   (a) possible geometry change.

−a		−a	−a
+s	−a	+s	−s
			−a
+a		+a	−s
+s	+s	+s	−a
		+s	−s

excited state = that of diene, but final product = that of olefin. Thus $\pi^* = as = A$

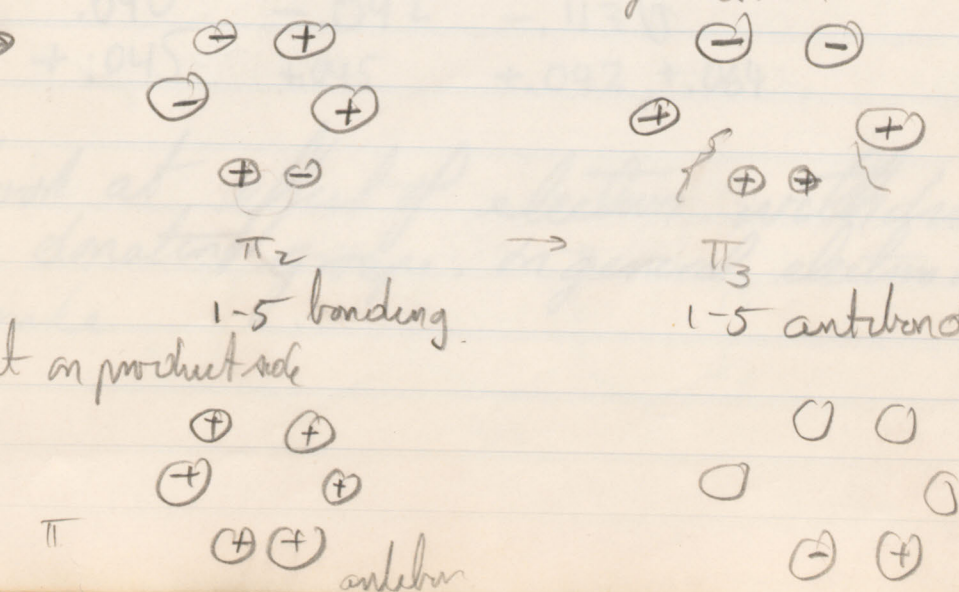
Then there is a crossing point

s— —a
a—s— with 2 configurations interacting

as ⟷ sa
aa ⟷ ss

only this matters

6. look at bond orders in excited state + charge distribution



orbital scheme →

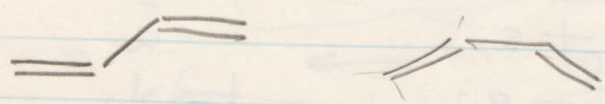
So far – 1. charge transfer

2. reluctance for 1,4 addition in *
(what about rotation mode)

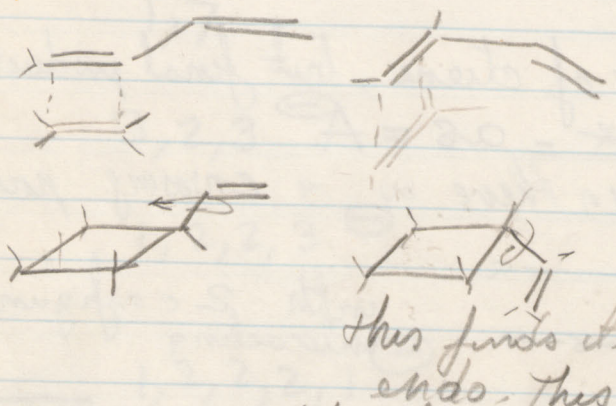
Look at charge distrib. in excited state. In particular which way does CT go. Is it reversed??

Still to be looked at is ≠ for 1,2 addition

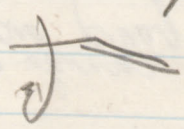
trans or cis?



π complex



thus finds itself endo. This doesn't perhaps seem like too much of a disadvantage since there appears to be free rotation of



Bad model chosen — should have $\chi_{\pi} \approx 2.05$ $C=C$

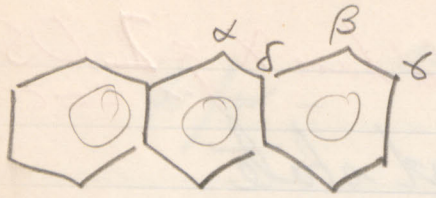
On charge transfer on ground state

at +3

π_2	→ ethylene	.0186
π	→ but	.2368
π_1	→ eth	.2510

		2.0	2.0	
	∞	−3	−2	0
	∞	3.20	2.29	Å
r				
π^*	16	8.238	8.216	7.775
	17	9.199	9.178	8.671
π_3				
π_2	18	12.473	12.466	12.110
π	19	13.218	13.156	12.387
$S_{\pi-\pi}$		0	−.0332	.1178
$n(1-5)$		0	.0026	.0345
1-2		1.2846	1.2829	1.2524
2-3		.8636	.8667	.9164
5-6		1.3050	1.3030	1.2640
$Q(1)$		−.137	−.133	−.049
2		+.013	+.009	−.082
5		−.090	−.092	−.113
$H_{7,8,9,10}$		+.045	+.045	+.042, +.064

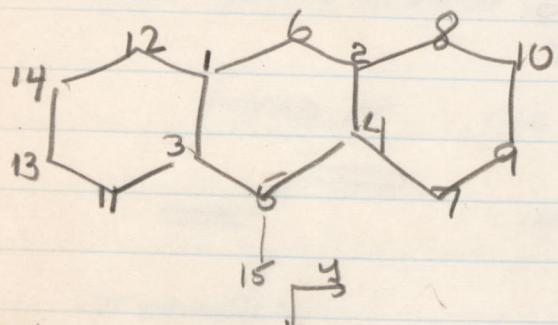
Look at effect of electron withdrawing + donating groups. In general electron withdrawing make



α β γ δ
5 7 9 1

	π	σ+π	π+ for 08	π⁻	Hückl.	exp ⊕	exp ⊖
α	−.031	+.152	.1945	.1792	.192	.289	.242
β	−.012	−.123	.0929	.0998	.096	.135	.119
γ	−.009	−.110	.0510	.0525	.047	.061	.068
δ	+.036	+.054	.0084	.0082			

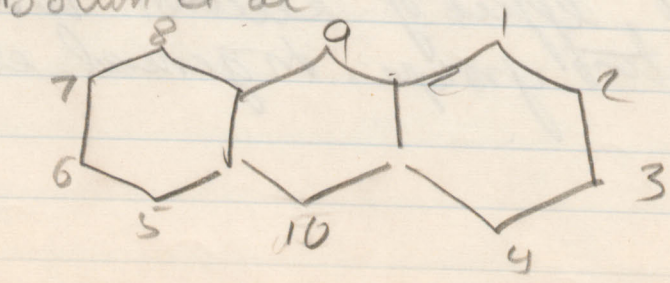
actual H charge .896 → .900



for 2

CH_3	+		+ averaged	− for 1
1,2	.0159, .0171	.0153, .0170	.0083	.0081
3,4	.0232, .0298	.0089, .0096	.0158	.0046
5	.3744	.3661	.1872	.1830
6	.4279	.3244	.2140	.1622
7,11	.1662, .1595	.2102, .2101	.0814	.1051
8,12	.1812, .1746	.1983, .2035	.0884	.1004
9,13	.1102, .1069	.0963, .1010	.0543	.0498
10,14	.0907, .0863	.1124, .1096	.0443	.0555
15	.0030	.0001	.0015	.0001
3 H_{CH_3} together	.0230	.0172	per H. .0077	.0057

Bolton et al



Bottom

	9	10	1	2	3	4
anth +	6.65	6.65	3.11	1.40	1.40	3.11
−	5.56	5.56	2.74	1.57	1.57	2.74
me anth +	7.79	7.03	2.81	1.46	1.19	2.85
−	4.27	5.16	2.94	1.39	1.73	2.77

ratio $\frac{\text{anthracene}}{\text{9 me}}$

+	0.90	1.14	0.94	1.15	1.05
−	1.10	0.95	1.06	0.95	0.99

	methyl a^+/a^-	methyl C	methyl X	mg a^+/a^-	mg C
+	1.82	1.02	1.35	1.36	1.32
−					

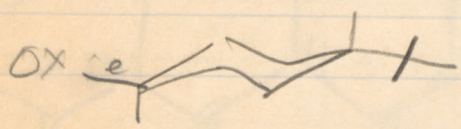
wrote to A McL Dec. 28

Shiner JACS 86, 945 (1964)

as-4-t-butylcyclohexyl

$\beta_a = 180°$ 1436
$\beta e = 60°$ 1.096

trans-4-t



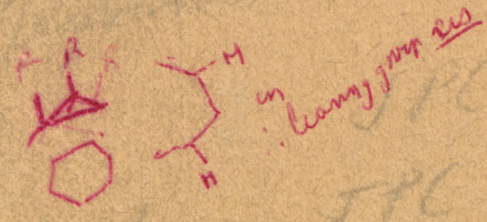
$\beta a = 60°$ 1.127
$\beta e = 60°$ 1.340
β eea = 2.087
β eeaa 2,425

products - 67% 4-t butylcyclohexene
27% t-butylcyclohexanols
6% ethers

olefin step involved loss of equat (trans) β-H

If only conformation sp^3 mattered a + e should be down. If sp^2 then equat in plane axial 60° out

con dos
hamno(s) contra


A
A
H
H
an
: bumpy ring sys