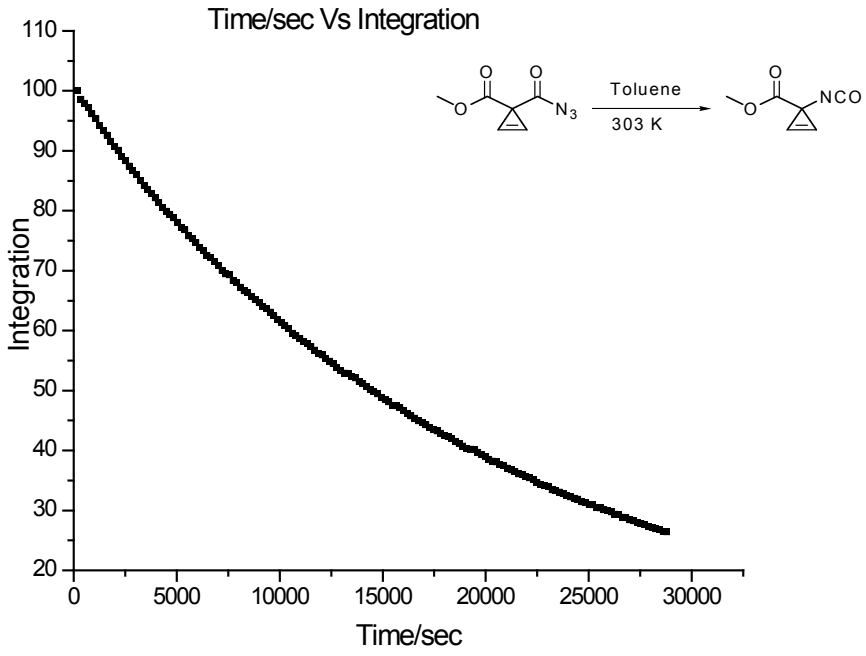
# The Curtius Rearrangement of Cyclopropyl- and Cyclopropenoyl Azides. A Combined Theoretical and Experimental Mechanistic Study

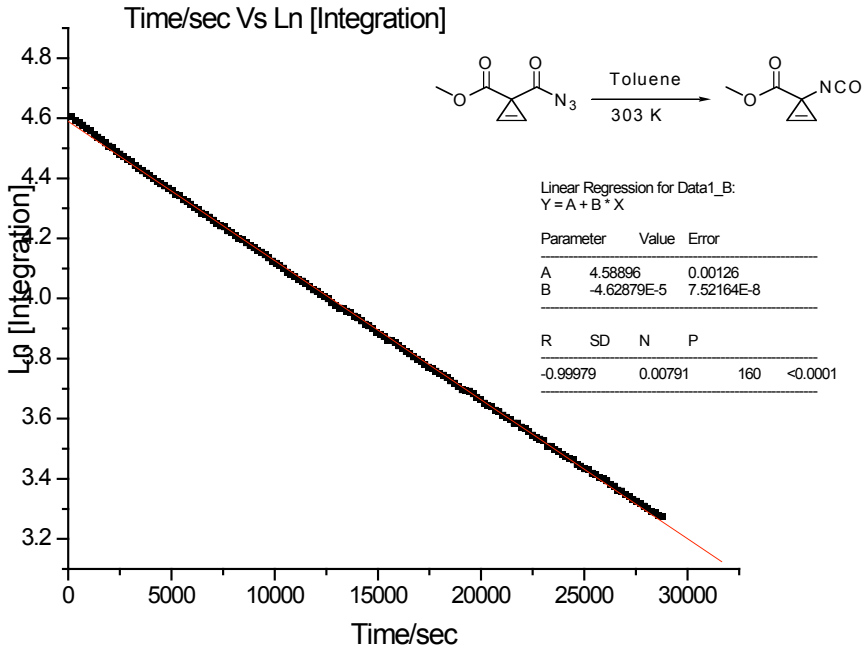
*Vinod Tarwade, Olga Dmitrenko, Robert D. Bach* and Joseph M. Fox**

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

Supporting Information

Kinetic plots for the Curtius Rearrangment of **1** at 303 K



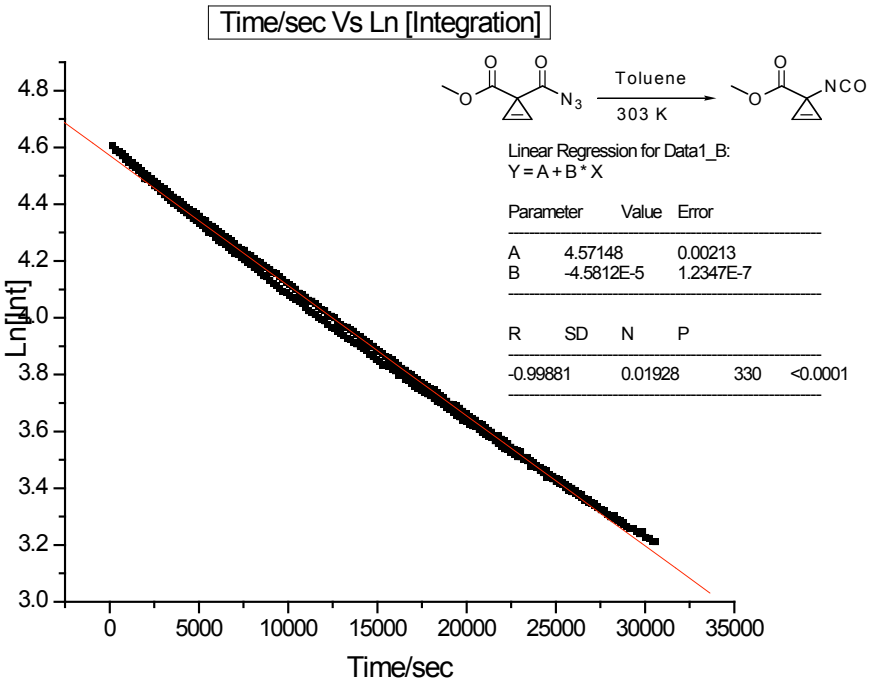




$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 4.63 \times 10^{-5}$: First Data Set

$k = 4.53 \times 10^{-5}$: Second Data Set

Error Analysis for the Curtius Rearrangment of **1** at 303 K

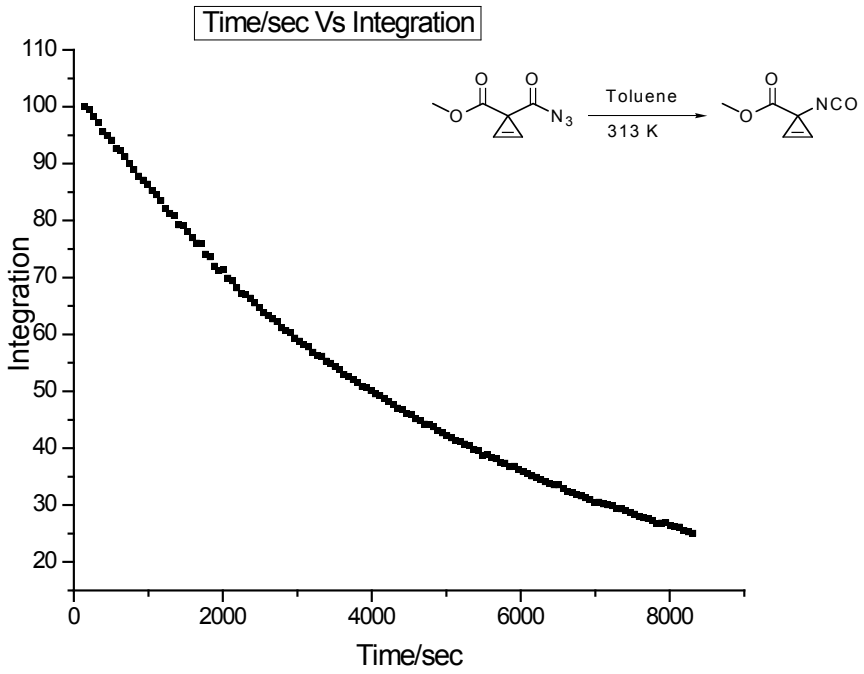


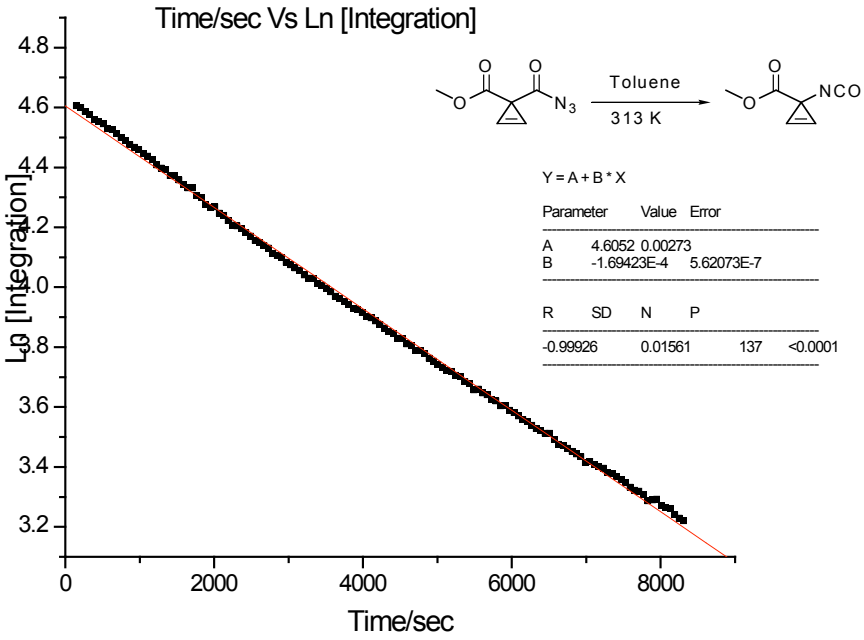

$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 4.58\ (0.22)^{a} \times 10^{-5}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Kinetic plots for the Curtius Rearrangment of **1** at 313 K



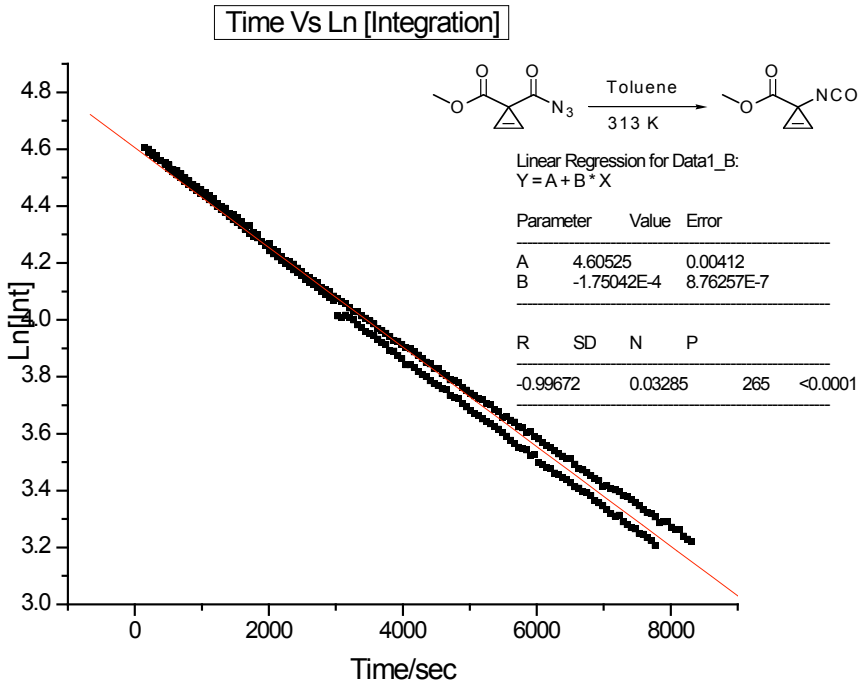




$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 1.69 \times 10^{-4}$: First Data Set

$k = 1.83 \times 10^{-4}$: Second Data Set

Error Analysis for the Curtius Rearrangment of **1** at 313 K

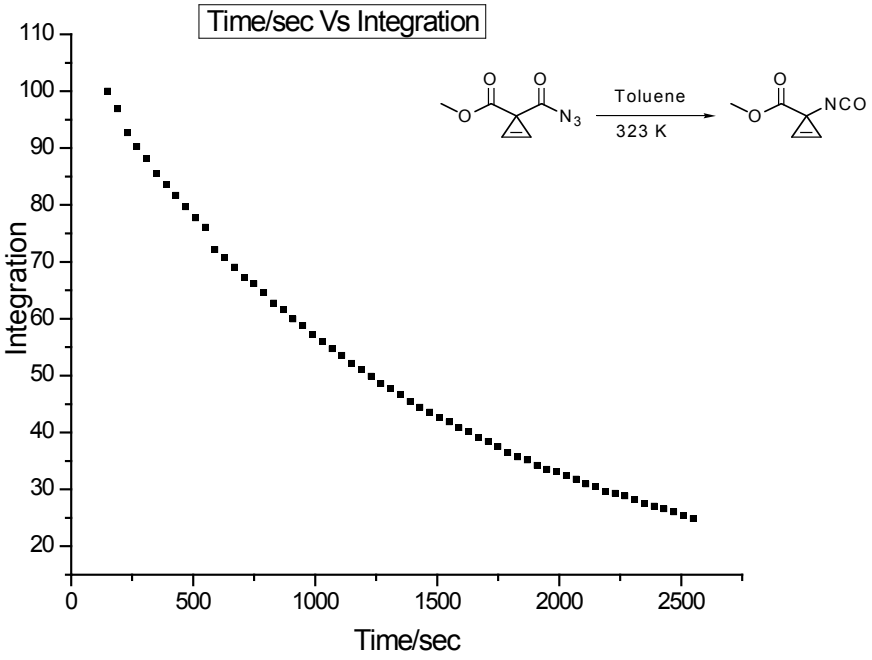


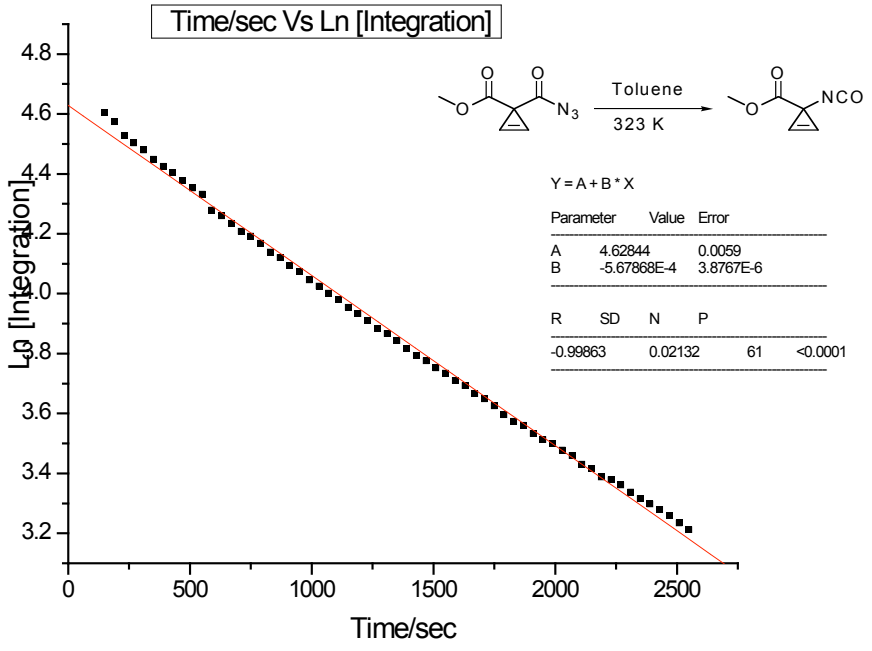

$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 1.75\ (0.14)^{a} \times 10^{-4}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Kinetic plots for the Curtius Rearrangment of **1** at 323 K



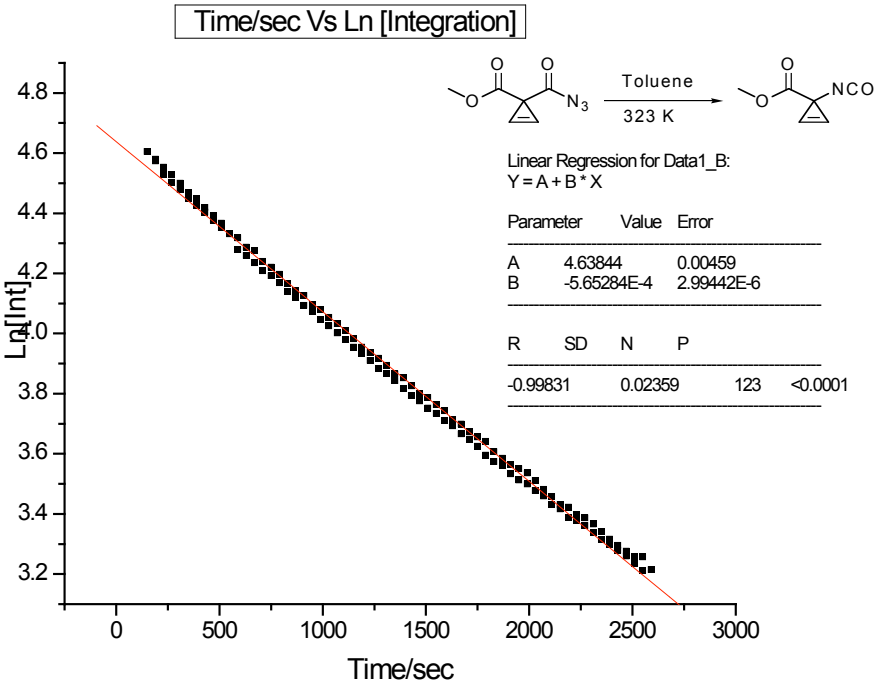




Ln [A] = – kt + Ln [$A_0$]

k = $5.68 \times 10^{-4}$: First Data Set

k = $5.63 \times 10^{-4}$: Second Data Set

Error Analysis for the Curtius Rearrangment of **1** at 323 K

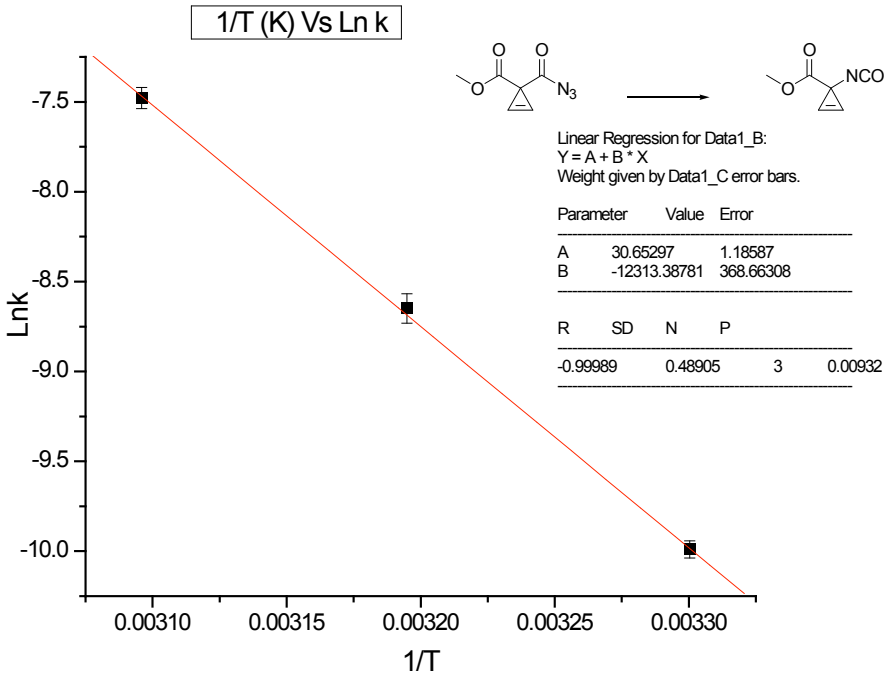



$Ln\,[A] = -kt + Ln\,[A_0]$

$k = 5.65\ (0.33)^{a} \times 10^{-4}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Arrhenius Plot for rearrangement of **1** to **2**




$$\text{Ln } k = -\frac{Ea}{R}\left(\frac{1}{T}\right) + \text{Ln } A$$

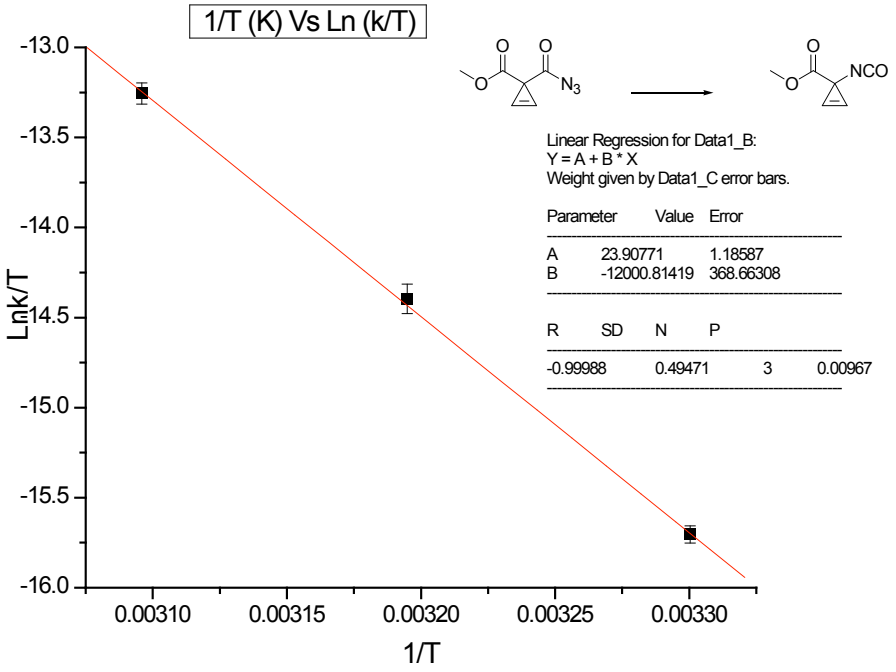
$$-\frac{Ea}{R} = -12313.39\ (637.78)^{a}$$

$$Ea = 102373.52\ (5302.95)\ \text{Joules/mol}$$

$$= 24.5\ (1.3)\ \text{Kcal/mol}$$

[a] The sample standard deviation is given in parenthesis, and was calculated from the Std. Error of the above plot.

Eyring Plot for rearrangement of **1** to **2**




$$\mathrm{Ln}\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right) + \mathrm{Ln}\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

$$-\frac{\Delta H^{\ddagger}}{R} = -12000.81\ (637.78)^{a}$$

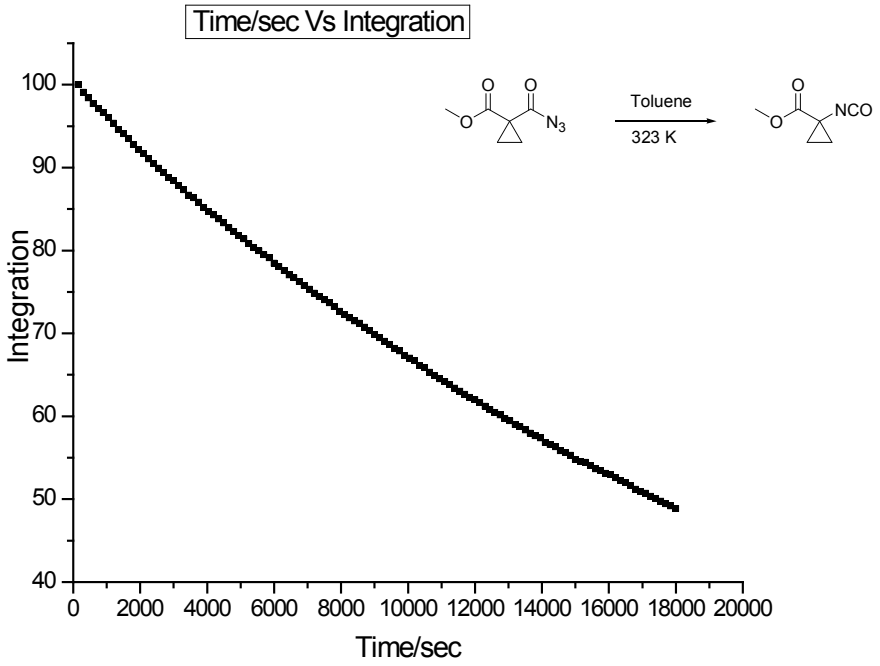
$$\Delta H^{\ddagger} = 99774.73\ (5298.04)\ \text{Joules/mol}$$

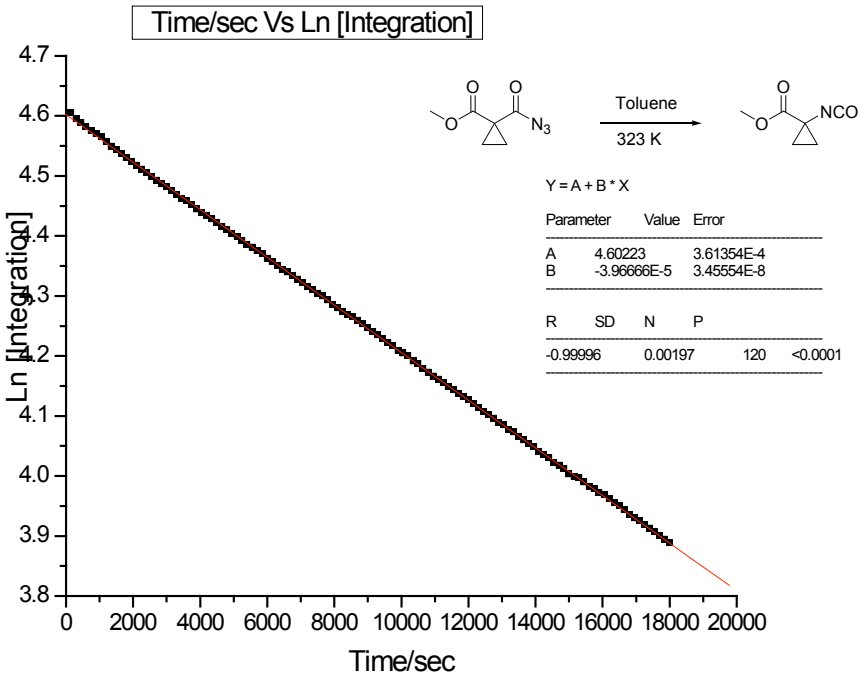
$$= 23.9\ (1.3)\ \text{Kcal/mol}$$

$$\Delta S^{\ddagger} = 0.28\ (4.08)\ \text{cal/mol/K}$$

[a] The sample standard deviation is given in parenthesis, and was calculated from the Std. Error of the above plot.

Kinetic plots for the Curtius Rearrangment of **3** at 323 K



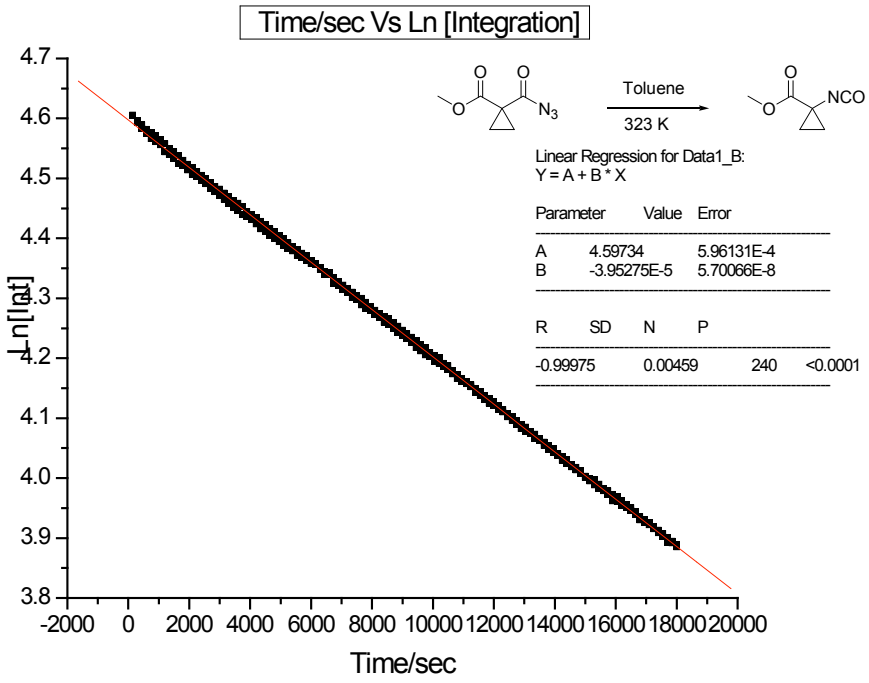




$Ln\,[A] = -\,kt + Ln\,[A_0]$

k = $3.97 \times 10^{-5}$: First Data Set

k = $3.94 \times 10^{-5}$: Second Data Set

Error Analysis for the Curtius Rearrangment of **3** at 323 K

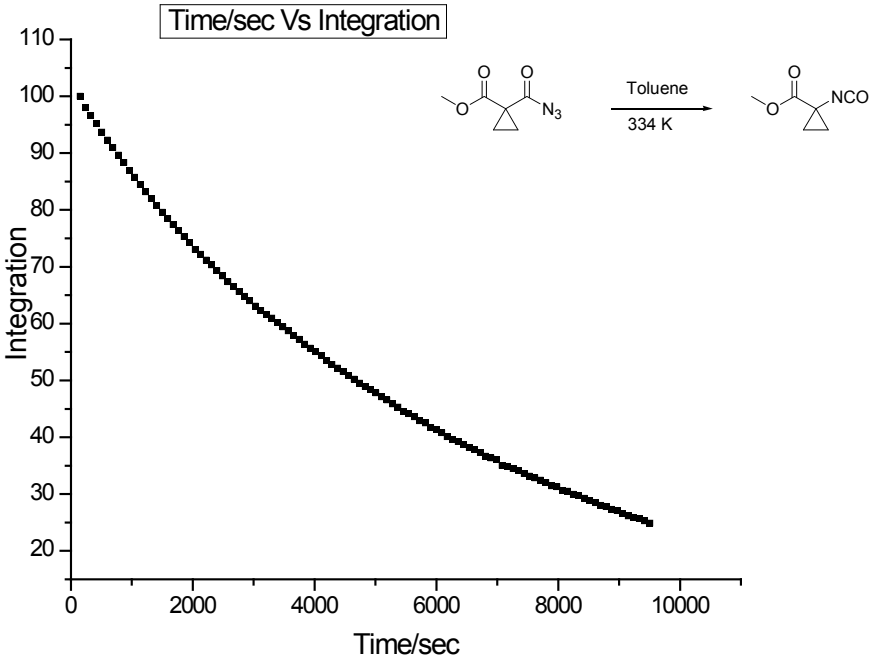


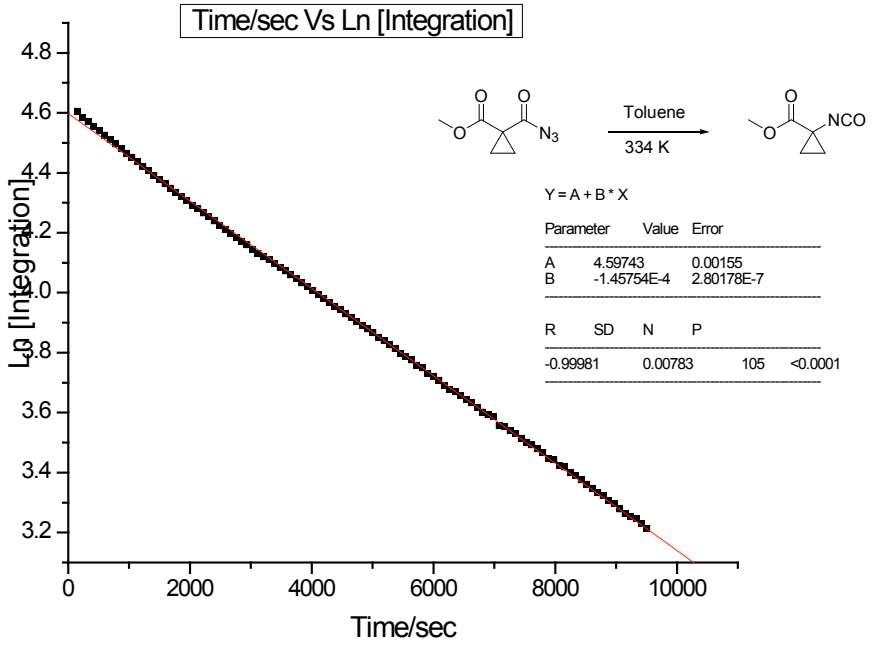

$Ln\,[A] = -kt + Ln\,[A_0]$

$k = 3.95\ (0.09)^{a} \times 10^{-5}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Kinetic plots for the Curtius Rearrangment of **3** at 334 K



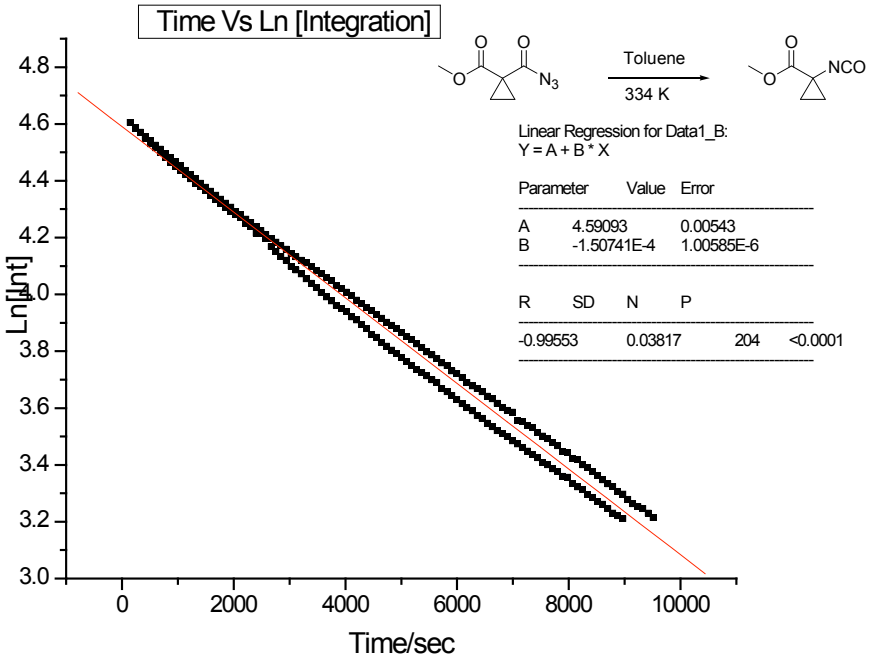




Ln [A] = – kt + Ln [$A_0$]

k = $1.46 \times 10^{-4}$: First Data Set

k = $1.58 \times 10^{-4}$: Second Data Set

Error Analysis for the Curtius Rearrangment of **3** at 334 K

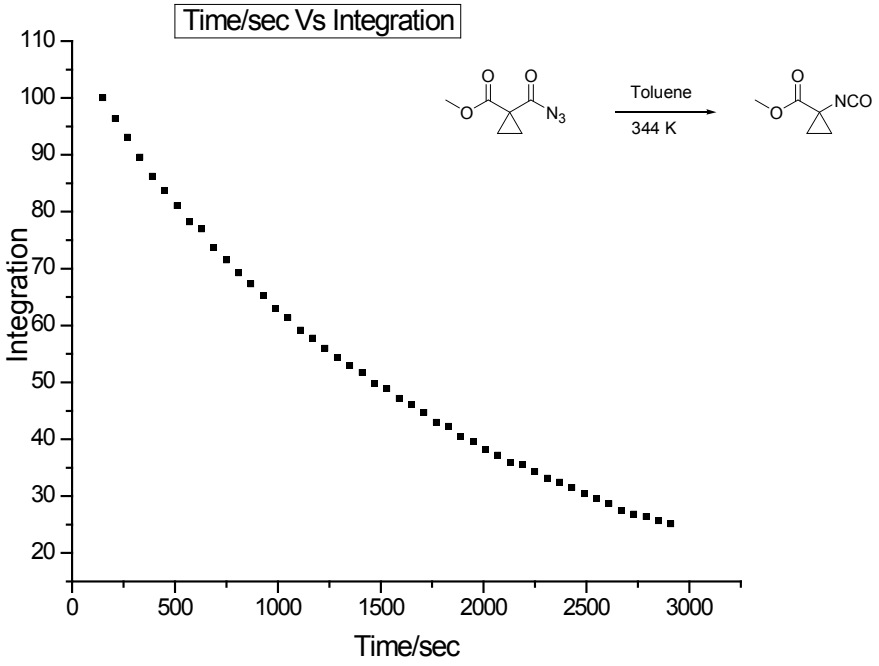


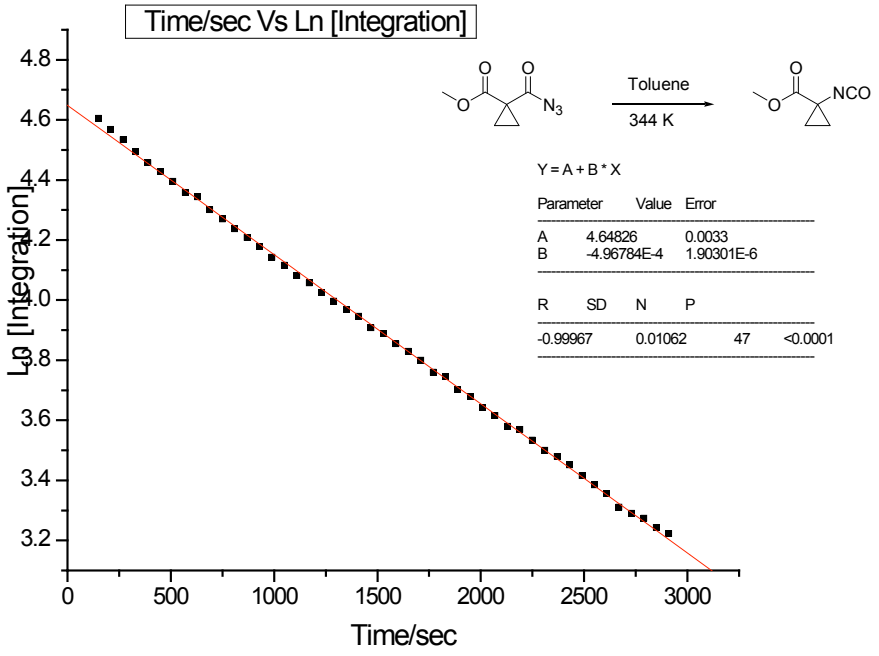

$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 1.51\ (0.14)^{a} \times 10^{-4}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Kinetic plots for the Curtius Rearrangment of **3** at 344 K



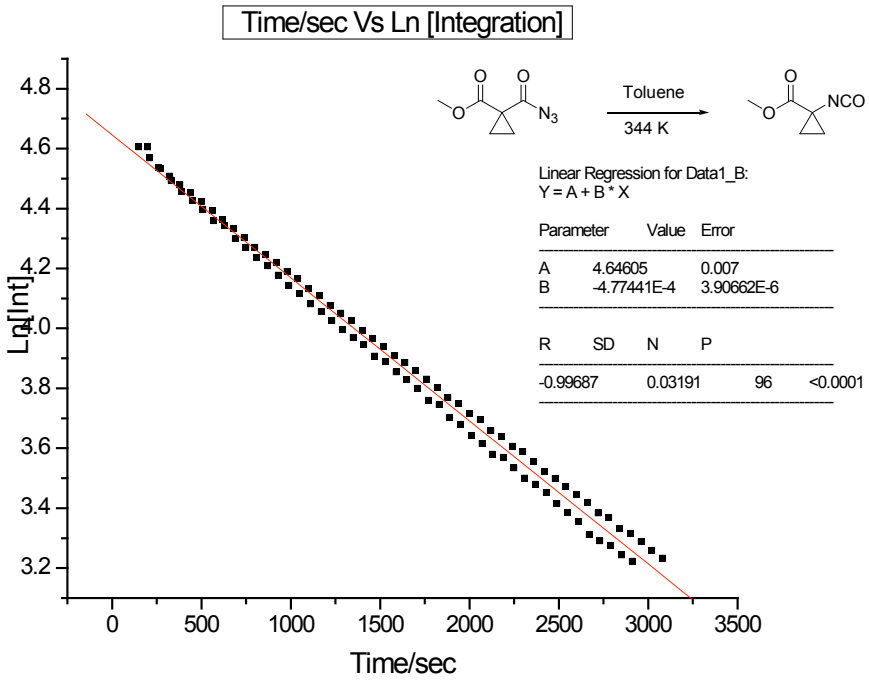




Ln [A] = – kt + Ln [$A_0$]

k = $4.97 \times 10^{-4}$: First Data Set

k = $4.64 \times 10^{-4}$: Second Data Set

Error Analysis of the kinetic plots for the Curtius Rearrangment of **3** at 344 K

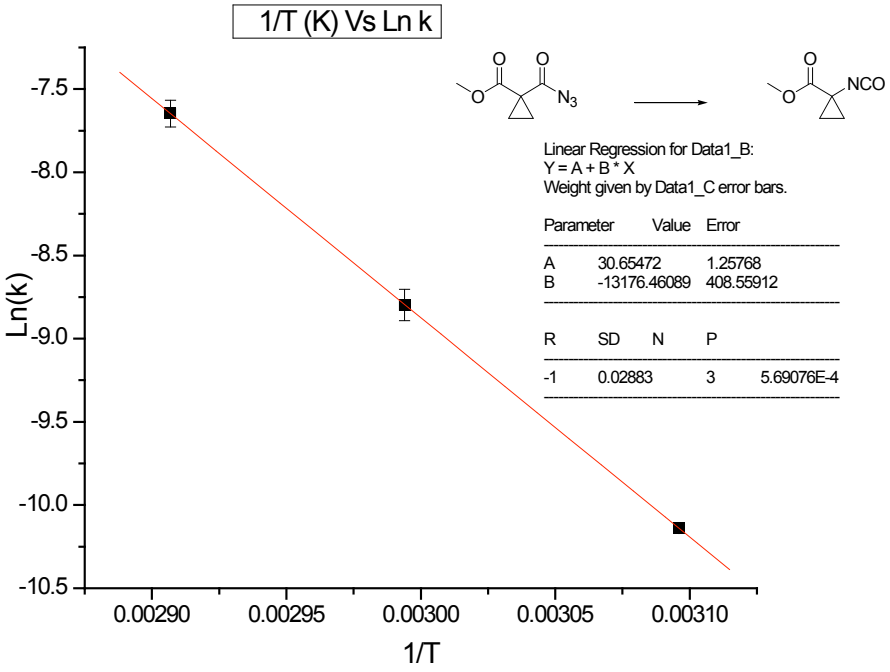



$Ln\,[A] = -\,kt + Ln\,[A_0]$

$k = 4.77\,(0.38)^{a} \times 10^{-4}$ : Average from two data sets.

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Arrhenius Plot for rearrangement of **3** to **4**




$$\text{Ln } k = \frac{-Ea}{R}\left(\frac{1}{T}\right) + \text{Ln } A$$

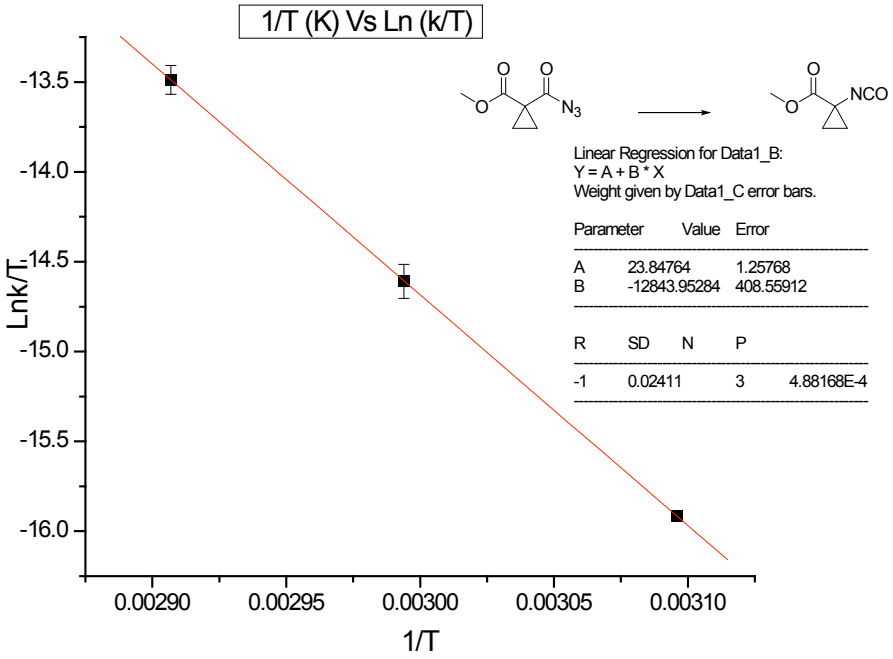
$$\frac{-Ea}{R} = -13176.46\ (706.81)^{a}$$

$$Ea = 109549.08\ (5871.83)\ \text{Joules/mol}$$

$$= 26.2\ (1.4)\ \text{Kcal/mol}$$

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.

Eyring Plot for rearrangement of **3** to **4**




$$\text{Ln}\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right) + \text{Ln}\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

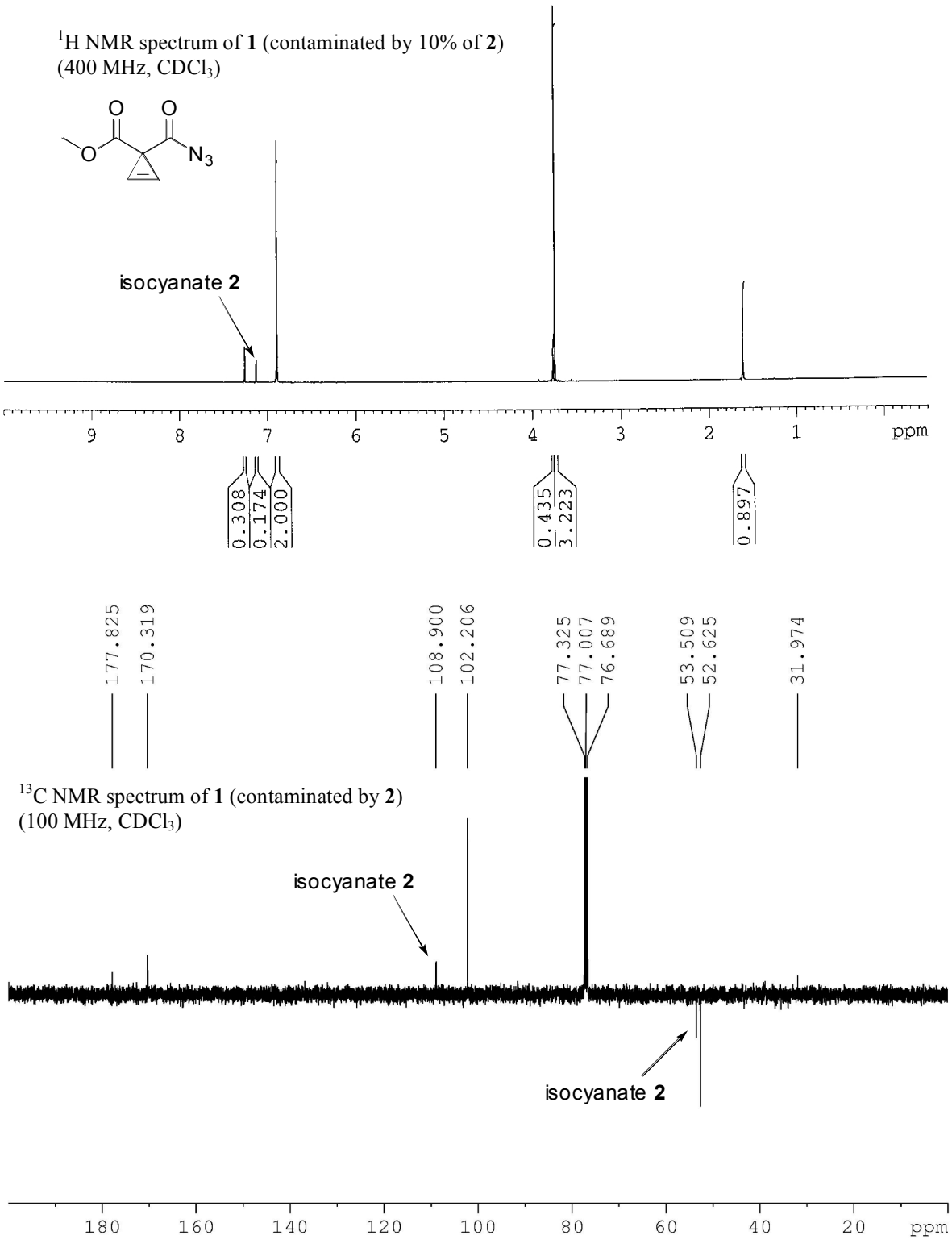
$$-\frac{\Delta H^{\ddagger}}{R} = -12843.95\ (706.81)^{a}$$

$$\Delta H^{\ddagger} = 106784.60\ (5873.15)\ \text{Joules/mol}$$

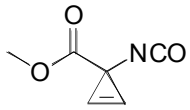
$$= 25.5\ (1.4)\ \text{Kcal/mol}$$

$$\Delta S^{\ddagger} = 0.18\ (4.47)\ \text{cal/mol/K}$$

[a] The sample standard deviation is given in parenthesis, and was calculated from the Standard Error of the above plot.


1H NMR spectrum of 1 (contaminated by 10% of 2)
(400 MHz, CDCl3)
O
O
O
N3
isocyanate 2
9
8
7
6
5
4
3
2
1
ppm
0.308
0.174
2.000
0.435
3.223
0.897
177.825
170.319
108.900
102.206
77.325
77.007
76.689
53.509
52.625
31.974
13C NMR spectrum of 1 (contaminated by 2)
(100 MHz, CDCl3)
isocyanate 2
isocyanate 2
180
160
140
120
100
80
60
40
20
ppm

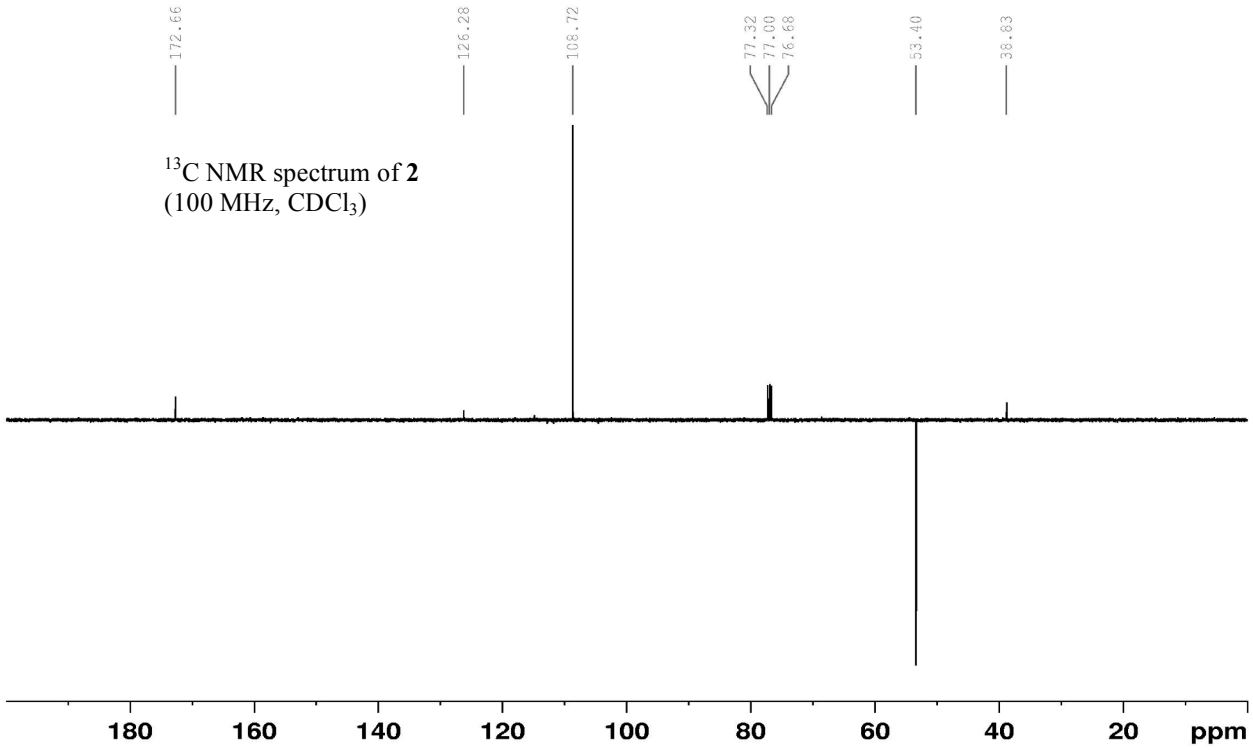
$^{1}$H NMR spectrum of **2**
(400 MHz, $CDCl_3$)



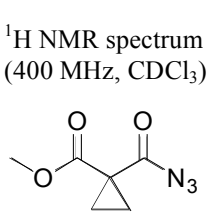




$^{13}$C NMR spectrum of **2**
(100 MHz, $CDCl_3$)



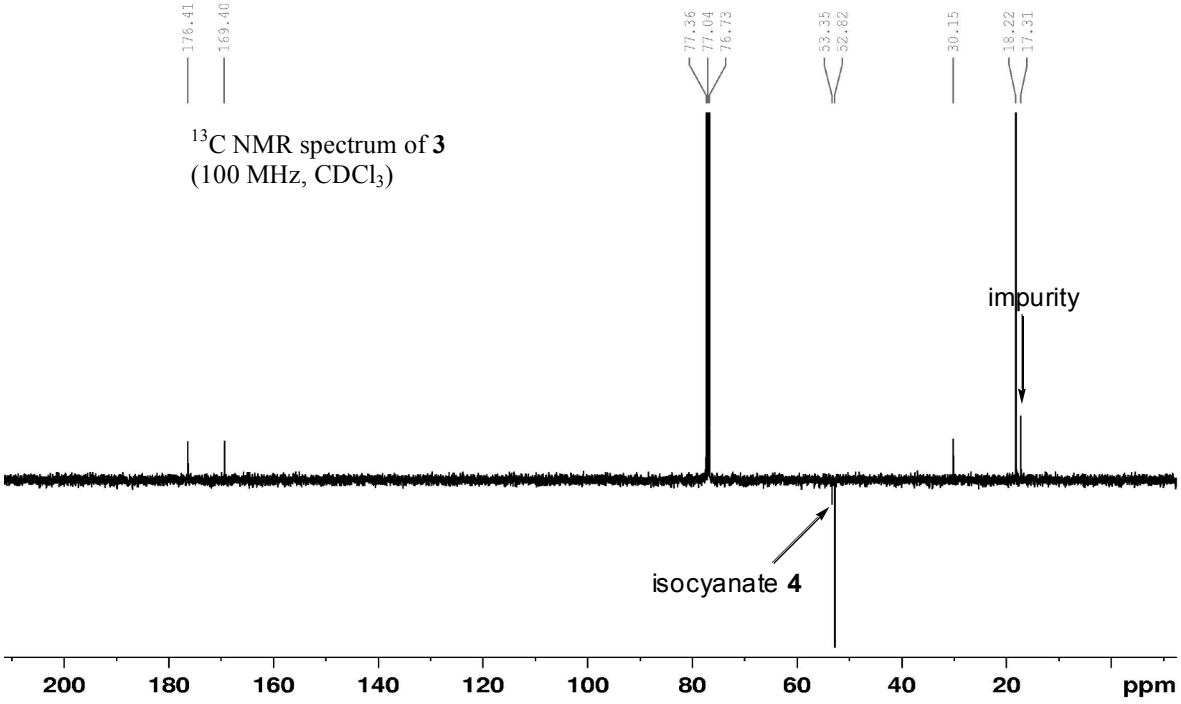
$^{1}$H NMR spectrum of **3**
(400 MHz, $CDCl_3$)

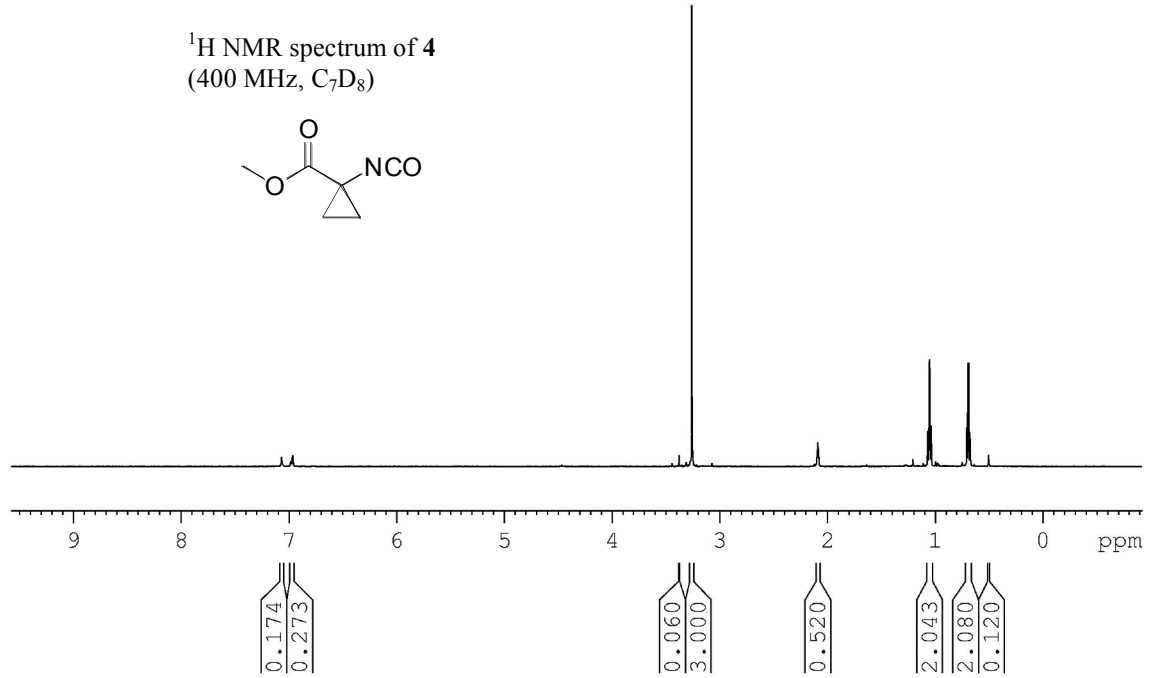


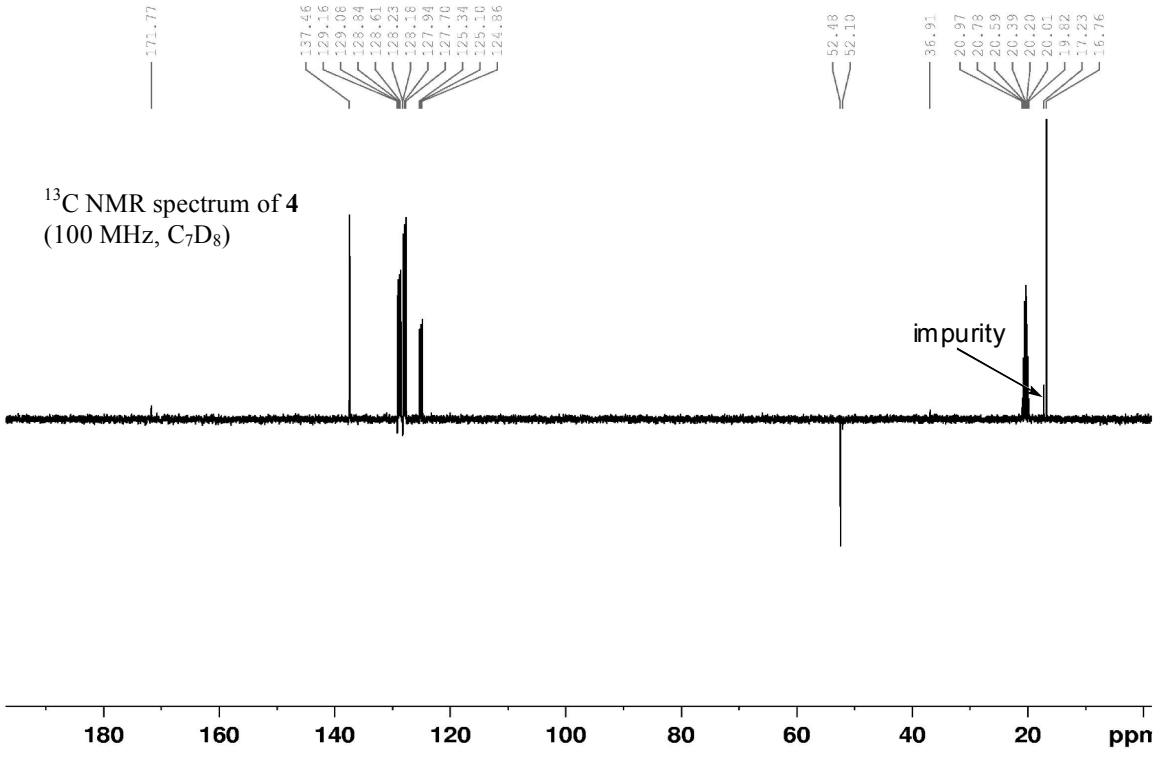




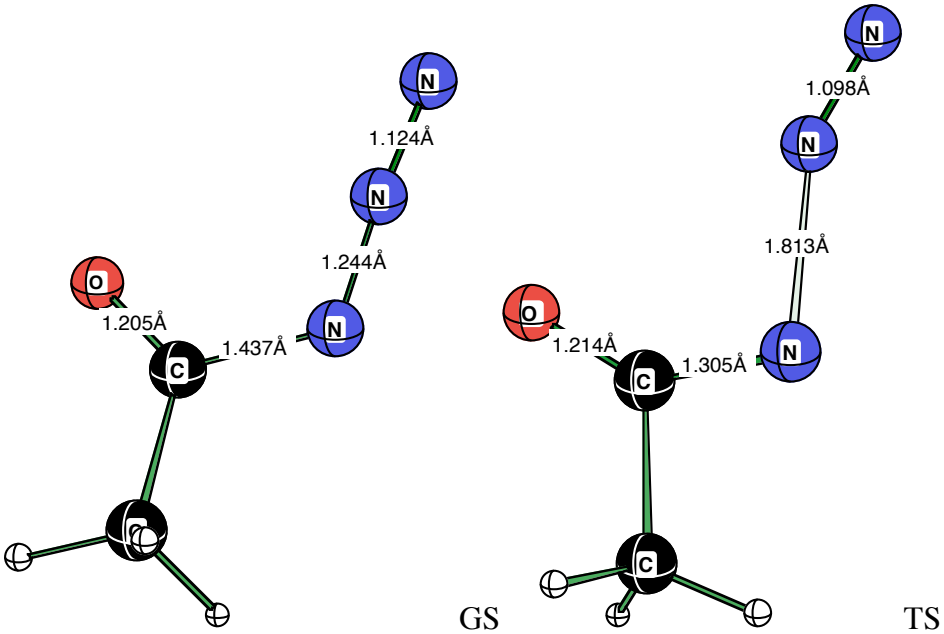
$^{13}$C NMR spectrum of **3**
(100 MHz, $CDCl_3$)




$^1$H NMR spectrum of **4**
(400 MHz, $C_7D_8$)
O
NCO
O
9
8
7
6
5
4
3
2
1
0
ppm
0.174
0.273
0.060
3.000
0.520
2.043
2.080
0.120


171.77
137.46
129.16
129.08
128.84
128.61
128.23
128.18
127.94
127.70
125.34
125.10
124.86
52.48
52.10
36.91
20.97
20.78
20.59
20.39
20.20
20.01
19.82
17.23
16.76
$^{13}$C NMR spectrum of **4**
(100 MHz, $C_7D_8$)
impurity
180
160
140
120
100
80
60
40
20
ppm

| acetyl azide | E, a.u. | DE, kcal/mol | ZPE, a.u. | Barrier, kcal/mol |
|---|---|---|---|---|
| GS | -317.53605 | 0 | -317.47647 | 0 |
| TS | -317.48788 | 30.23 | -317.43257 | 27.55 |




GS TS

Acetyl azide Ground State RB3LYP/6-311+G(d,p)
Charge = 0 Multiplicity = 1

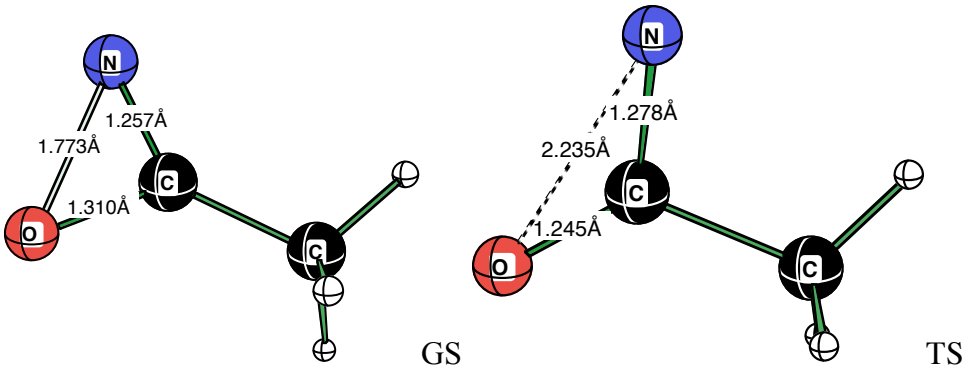
| | |
|---|---|
| C | -0.1008821349,-0.4337590153,2.1324000592 |
| C | 0.2771148443,0.0292130228,0.7528035242 |
| O | 1.2657367481,0.6556413803,0.4655023133 |
| N | -0.7074367443,-0.3747216005,-0.2120992967 |
| N | -0.4663964442,-0.0287584473,-1.3826828007 |
| N | -0.3365538708,0.2375739932,-2.4671575834 |
| H | 0.6619567099,-0.1194735796,2.8413826112 |
| H | -0.2017139272,-1.5218412926,2.1447825862 |
| H | -1.0708236086,-0.0151978327,2.4121725615 |

Acetylazide Transition Structure for loss of $N_2$
RB3LYP/6-311+G(d,p) Im. Freq=509.2867i $cm^{-1}$
Charge = 0 Multiplicity = 1

| | |
|---|---|
| C | -0.6542828072,0.0323763365,-2.1447463174 |
| H | -1.7160329973,0.2473457038,-2.0375825744 |
| C | 0.1796595321,-0.0714865305,-0.7983621182 |
| O | 1.3701225614,-0.304818668,-0.7629164407 |
| N | -0.8016824287,0.1595451938,0.0304585121 |

| | | | | |
|---|---|---|---|---|
| N | -0.0117817893,0.0767784111,1.6604555812 | | | |
| N | -0.0022744881,0.1253664568,2.7570885282 | | | |
| H | -0.518013134,-0.9351393504,-2.6279645244 | | | |
| H | -0.1690237666,0.8291737225,-2.7084891127 | | | |

| acetyl nitrene | E, a.u. | DE, kcal/mol | ZPE, a.u. | Barrier, kcal/mol |
|---|---|---|---|---|
| GS | -207.93650 | 0 | -207.88851 | 0 |
| TS | -207.91217 | 15.26 | -207.86662 | 13.74 |




GS TS

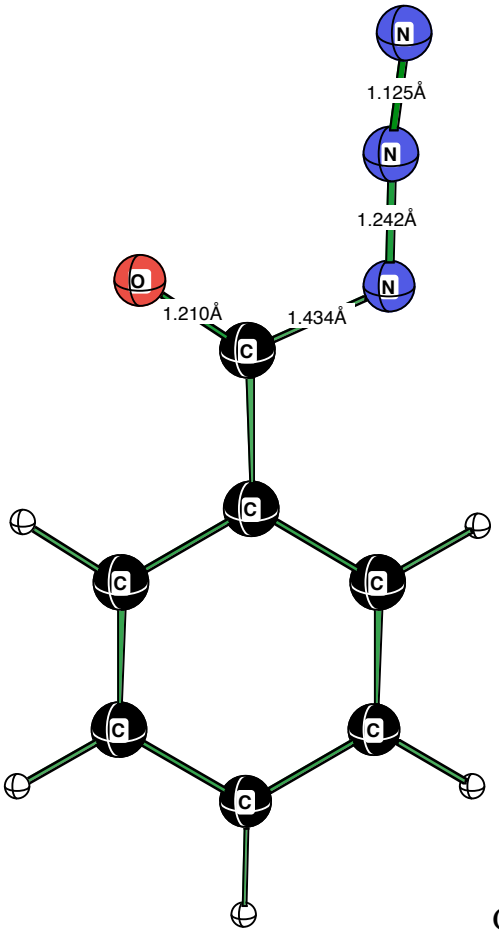
acetylnitrene ground state RB3LYP/6-311+G(d,p)
Charge = 0 Multiplicity = 1

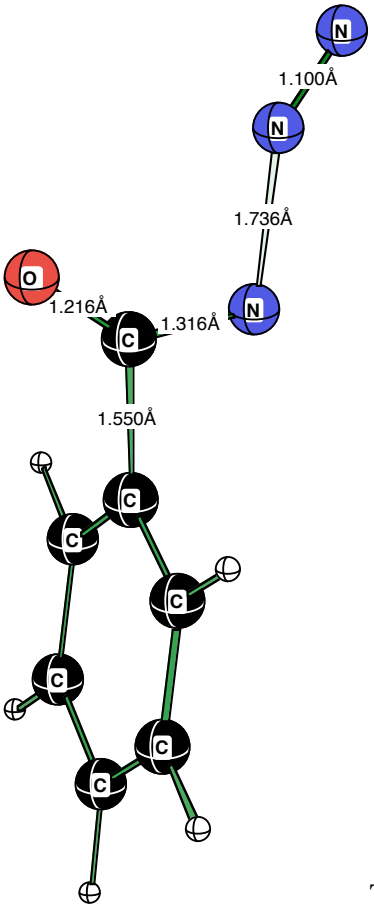
| | |
|---|---|
| C | 0.0187463478,0.0000044098,0.0801360432 |
| O | -1.1956412404,-0.0000088949,-0.4112473716 |
| N | -0.5055188656,-0.0000195142,1.2221614571 |
| C | 1.3362987217,0.0000188468,-0.5789800018 |
| H | 2.1384315569,0.0000263888,0.1591605889 |
| H | 1.4175407738,-0.8847154902,-1.2156258222 |
| H | 1.4175192349,0.8847573205,-1.2156222424 |

Acetylazide transition state (nitrene rearrangment to isocyanate) RB3LYP/6-311+G(d,p)
Im. Freq.= 890.9822i $cm^{-1}$
Charge = 0 Multiplicity = 1

| | |
|---|---|
| C | -0.6153974024,-0.0000122771,1.1837451189 |
| H | -1.7077974223,-0.001151382,1.0908360035 |
| C | 0.1157286307,-0.0000154801,-0.1680907365 |
| O | 1.3432579332,-0.0007586467,-0.3759907167 |
| N | -0.7767701588,0.0008719897,-1.0834265262 |
| H | -0.3023169167,0.9084817689,1.7029172485 |
| H | -0.3005453855,-0.9071985988,1.704231871 |

| benzoyl azide | E, a.u. | DE, kcal/mol | ZPE, a.u. | Barrier, kcal/mol |
|---|---|---|---|---|
| GS | -509.32046 | 0 | -509.20717 | 0 |
| TS | -509.26783 | 33.03 | -509.15931 | 30.03 |



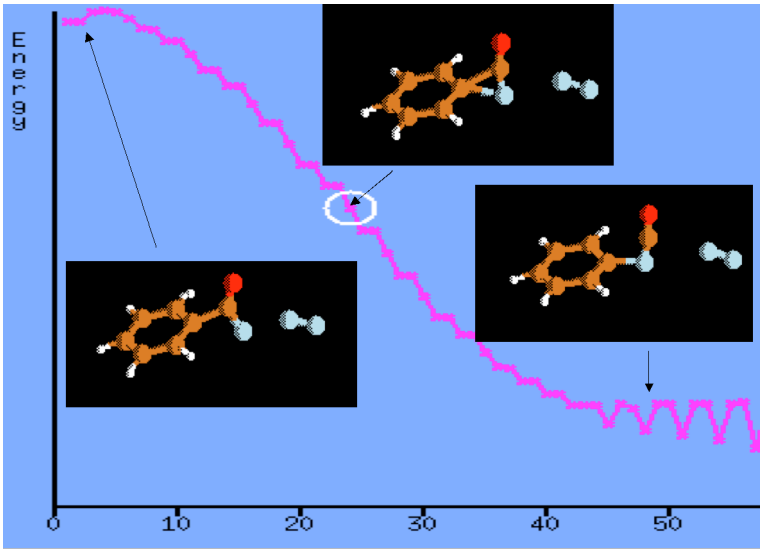

GS TS

Ground state for Benzoylazide RB3LYP/6-311+G(d,p)
Charge = 0 Multiplicity = 1

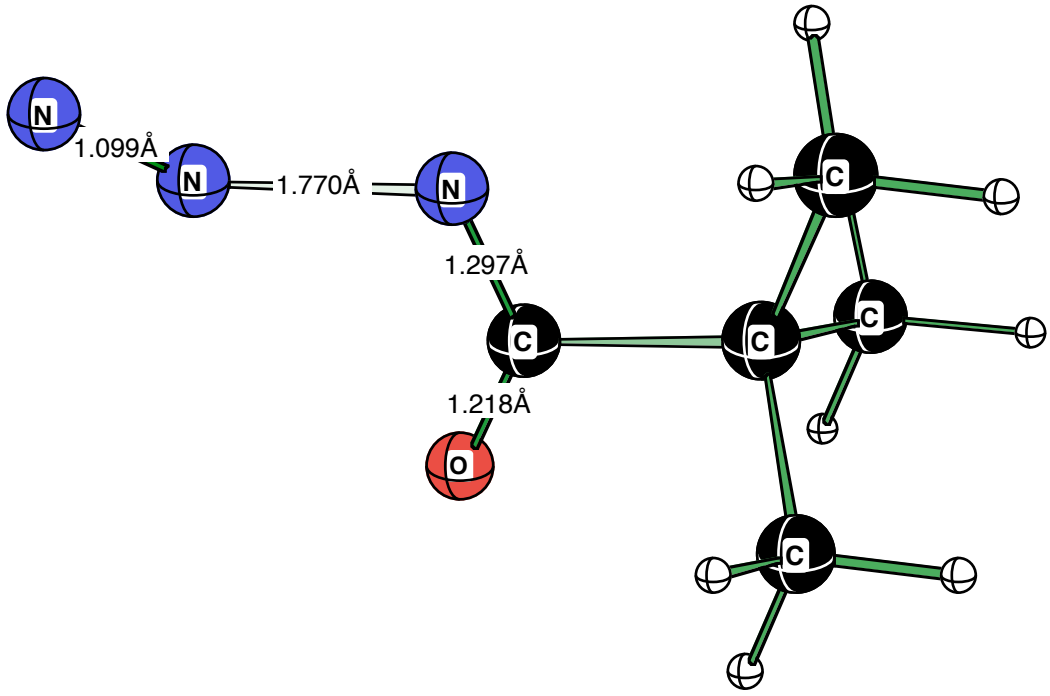
| | |
|---|---|
| C | 0.6144195785,-0.0173132894,-0.8644780145 |
| O | 1.7923054917,0.0155416947,-1.1402054572 |
| N | -0.412426133,-0.1058561597,-1.8620588042 |
| N | 0.0009977712,-0.1461753105,-3.0322045754 |
| N | 0.2764912927,-0.1884957059,-4.1218271732 |
| C | 0.0659916197,0.0274469945,0.5146191912 |
| C | -1.3090746235,-0.0142329212,0.7770709178 |
| C | -1.7665887348,0.0311099551,2.0904918362 |
| C | -0.8581024262,0.1179049428,3.1449035948 |
| C | 0.5130455022,0.1596892229,2.8866657438 |
| C | 0.9753945112,0.1146854394,1.5770651093 |
| H | -2.009500971,-0.0813280406,-0.0452151252 |
| H | -2.8311186061,-0.001349111,2.2915783018 |

H -1.2175586504,0.1529936138,4.1672922154
H 1.2186896614,0.2273274555,3.7065680566
H 2.0350915544,0.1459706923,1.3560238075

Transition state for rearrangement of benzoylazide RB3LYP/6-311+G(d,p)
Im. Freq=569.3065i $cm^{-1}$
Charge = 0 Multiplicity = 1
C 0.1641858003,0.5194430258,-0.9931772678
O 0.3727989079,1.6300074447,-1.4413979835
N 0.0168557994,-0.7019257224,-1.4606204718
N 0.1834295546,-0.5659063079,-3.1831504173
N 0.2013794645,-1.0117973422,-4.1884610283
C -0.0173216182,0.1653920007,0.5049394539
C -1.2869814368,0.2467102831,1.0827879914
C -1.42242024,0.1027397001,2.4602156652
C -0.2990140403,-0.143843296,3.250340656
C 0.9635606456,-0.2489371103,2.6653530976
C 1.1072485093,-0.1062253079,1.2886934652
H -2.153444531,0.4321224477,0.4592029113
H -2.4029518821,0.1757345308,2.916257265
H -0.4085676627,-0.2617732729,4.3224264007
H 1.8333134445,-0.4485247186,3.2805264974
H 2.0820599196,-0.1918887109,0.8234758461

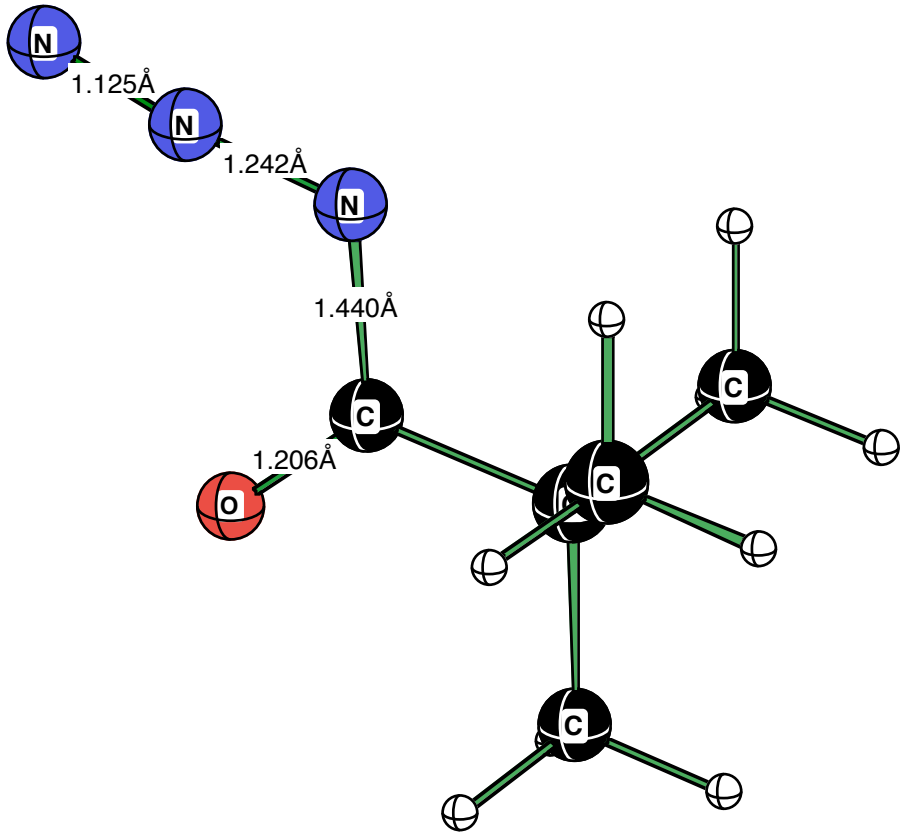


| pivaloyl azide | E, a.u. | DE, kcal/mol | ZPE, a.u. | Barrier, kcal/mol |
|---|---|---|---|---|
| TS | -435.46065 | 0 | -435.32111 | 0 |
| GS | -435.50857 | 30.07 | -435.36472 | 27.36 |




Transition state for rearrangment of pivaloyl azide: RB3LYP/6-311+G(d,p)
Im.Freq=542.5040icm-1
Charge = 0 Multiplicity = 1

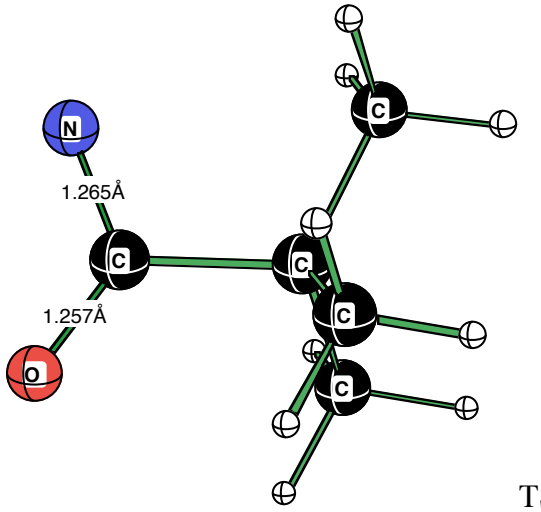
| | |
|---|---|
| C | -0.161686149,0.0231402662,-1.2816712965 |
| C | 0.2923136843,0.3045534338,0.2695543937 |
| O | 1.0752379722,1.196359527,0.5417195591 |
| N | -0.3765008666,-0.6047911539,0.9090632609 |
| N | 0.0656875668,-0.3620480147,2.6052650347 |
| N | -0.0130872077,-0.6360096138,3.6669212333 |
| C | 1.1664630306,-0.260102783,-1.9994210177 |
| H | 1.6102369312,-1.1986490305,-1.6574641534 |
| H | 0.9740932562,-0.3507748387,-3.0734780395 |
| H | 1.8822797018,0.545591449,-1.8356061566 |
| C | -1.1550299863,-1.1237578885,-1.5359980743 |
| H | -1.3514935213,-1.1770324862,-2.6122289925 |
| H | -0.7566697559,-2.0883421237,-1.217944687 |
| H | -2.1064539693,-0.9615470888,-1.0273218058 |
| C | -0.7742839564,1.3600248441,-1.7253323371 |
| H | -0.0818718673,2.1852574258,-1.5582128472 |
| H | -1.0074391592,1.3034001242,-2.793629284 |
| H | -1.7039415805,1.5680145945,-1.1894072171 |




Ground state for pivaloyl azide RB3LYP/6-311+G(d,p)
Charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -0.0724768022 | 1.2112859646 | -0.2260753675 |
| C | -0.0258215769 | -0.1632797295 | 0.4434740428 |
| O | -0.1117226916 | -0.3753632964 | 1.6270746085 |
| N | 0.1375250547 | -1.2213578603 | -0.5198320845 |
| N | 0.1827457087 | -2.3646034897 | -0.0374452422 |
| N | 0.2337635051 | -3.4329359903 | 0.311681865 |
| C | -0.2474181988 | 2.2833477091 | 0.8594351188 |
| H | 0.5795311419 | 2.2657918381 | 1.5718438264 |
| H | -0.2823413298 | 3.2717511161 | 0.3939464096 |
| H | -1.1713977024 | 2.132861503 | 1.4209468684 |
| C | 1.2489037354 | 1.4401609209 | -0.9934649798 |
| H | 1.2272639453 | 2.426942019 | -1.4642826567 |
| H | 2.1088981796 | 1.408594098 | -0.3187413882 |
| H | 1.3952899617 | 0.6913092375 | -1.7736729838 |
| C | -1.2632042725 | 1.2494408923 | -1.2099602175 |
| H | -2.2108569984 | 1.0806344756 | -0.6910213136 |
| H | -1.3099178985 | 2.2343192972 | -1.6829368219 |
| H | -1.1608249564 | 0.497249625 | -1.9939621574 |

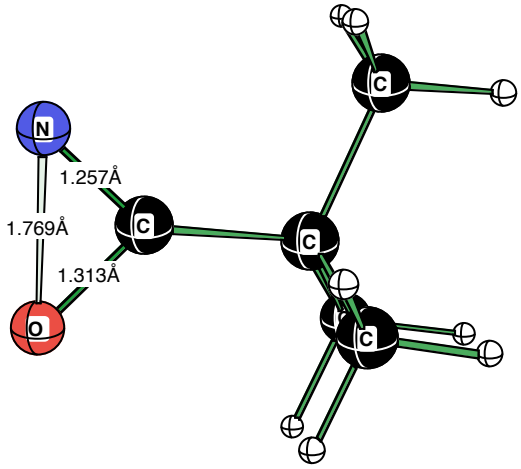
| pivaloylnitrene | E, a.u. | DE, kcal/mol | ZPE, a.u. | Barrier, kcal/mol |
|---|---|---|---|---|
| TS | -325.88811 | 0 | -325.75833 | 0 |
| GS | -325.91154 | 14.70 | -325.77927 | 13.14 |




TS

pivaloyl nitrene (t-butyl acyl nitrene ) t-butyl rearr TS
RB3LYP/6-311+G(d,p) Im.Freq= -946.5931i $cm^{-1}$
Charge = 0 Multiplicity = 1

| | |
|---|---|
| C | 0.0525550135,-0.000025495,-1.0532546009 |
| O | -0.9608420698,0.0000474075,-1.7966667515 |
| N | 1.2370355178,-0.00013625,-1.4965652923 |
| C | 0.0118213752,0.0000094307,0.5335938132 |
| C | 1.4015395644,-0.0000994978,1.197099575 |
| H | 1.9817323668,0.8866603046,0.9318876811 |
| H | 1.2726883608,-0.0000665111,2.2834475614 |
| H | 1.9815764069,-0.8869718489,0.9319229465 |
| C | -0.7696168631,-1.2745734541,0.8895777633 |
| H | -0.2037813486,-2.1740988355,0.6364205737 |
| H | -0.9510597406,-1.2790923978,1.9701608847 |
| H | -1.730550437,-1.3069704949,0.3748968575 |
| C | -0.7693928787,1.2747436892,0.8895274603 |
| H | -0.9508341253,1.2793376788,1.9701105427 |
| H | -0.2033996385,2.1741595933,0.636333897 |
| H | -1.730321179,1.3072889635,0.3748460474 |



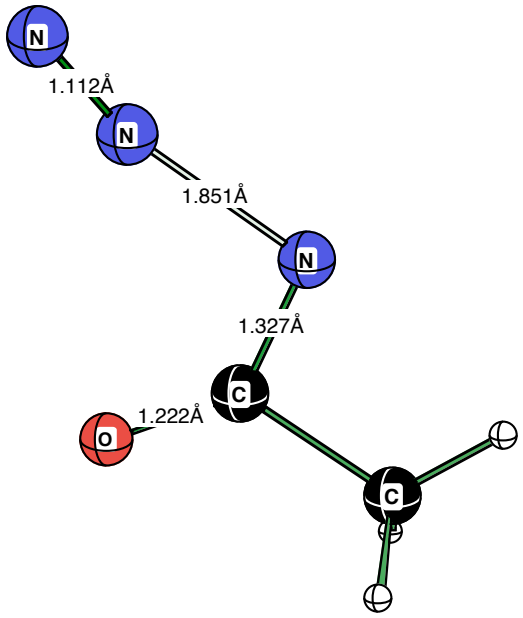

ground state for pivaloyl nitrene
RB3LYP/6-311+G(d,p)
Charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | 0.1323592365 | 0.0001604157 | 0.9083624674 |
| O | -0.7687435476 | 0.0007397766 | 1.8637085384 |
| N | 0.9994266014 | -0.0000627202 | 1.8189298919 |
| C | 0.0011770329 | -0.0001140043 | -0.578041258 |
| C | 1.4047050583 | -0.0007742358 | -1.2060868376 |
| H | 1.9728353352 | -0.8863485605 | -0.910295116 |
| H | 1.3204605072 | -0.0010226533 | -2.2956406135 |
| H | 1.9734767446 | 0.8845359287 | -0.9107399343 |
| C | -0.7867127034 | 1.2665778569 | -0.979228659 |
| H | -0.2473167624 | 2.1743063179 | -0.6983037536 |
| H | -0.9304569226 | 1.273901955 | -2.0626790604 |
| H | -1.7685973917 | 1.2895780798 | -0.501909379 |
| C | -0.7876335629 | -1.2664179659 | -0.9786519016 |
| H | -0.9313751509 | -1.2741319448 | -2.0620999421 |
| H | -0.2488981274 | -2.1744079006 | -0.6973059124 |
| H | -1.7695364293 | -1.2884827925 | -0.5013267064 |

Recover connectivity data from disk.

dinitrogen (N2)
RCCSD(FC)/6-31G(d)
R(1,2) 1.1135 Å
RCCSD-FC\6-311+G(d,p)
R(1,2) 1.1032
Zero-point correction= 0.005487 (Hartree/Particle)
Thermal correction to Energy= 0.007847
Thermal correction to Enthalpy= 0.008791
Thermal correction to Gibbs Free Energy= -0.012959
Sum of electronic and zero-point Energies= -109.294584
Sum of electronic and thermal Energies= -109.292224
Sum of electronic and thermal Enthalpies= -109.291280
Sum of electronic and thermal Free Energies= -109.313030

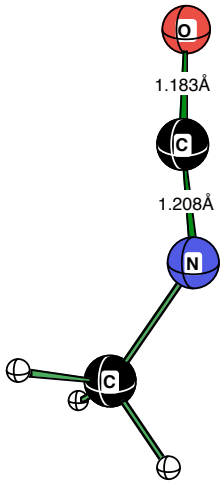
SP\RCCSD(T)-FC\6-311+G(d,p)\N2:
CCSD(T)=-109.315077 a.u.




transition state for rearrangment of acetylazide to methyl isocyanate
RCCSD-FC\6-31G(d)= -316.519603 a.u.

| | | | |
|---|---|---|---|
| 6 | 0.139192 | 0.000474 | -0.784629 |
| 8 | 1.348705 | 0.001709 | -0.611308 |
| 7 | -0.936668 | -0.000827 | -0.008019 |
| 6 | -0.555934 | 0.000031 | -2.178746 |
| 1 | -1.649496 | -0.001182 | -2.150968 |
| 1 | -0.202365 | 0.897827 | -2.692981 |
| 1 | -0.200380 | -0.896745 | -2.693390 |
| 7 | -0.142115 | -0.000448 | 1.663285 |
| 7 | 0.097721 | -0.000648 | 2.748670 |

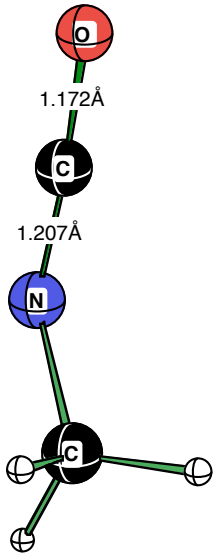
---




methylisocyanate
\FOpt\RCCSD-FC\6-31G(d)= -207.3930527

| | | | |
|---|---|---|---|
| 6 | -0.850791 | 0.018293 | -0.924161 |
| 1 | -1.863962 | 0.363325 | -1.142194 |
| 6 | 0.303825 | -0.002364 | 1.264156 |
| 8 | 1.103334 | -0.142909 | 2.125005 |
| 7 | -0.602784 | 0.197922 | 0.491087 |
| 1 | -0.769830 | -1.038265 | -1.201873 |
| 1 | -0.142193 | 0.603796 | -1.520039 |

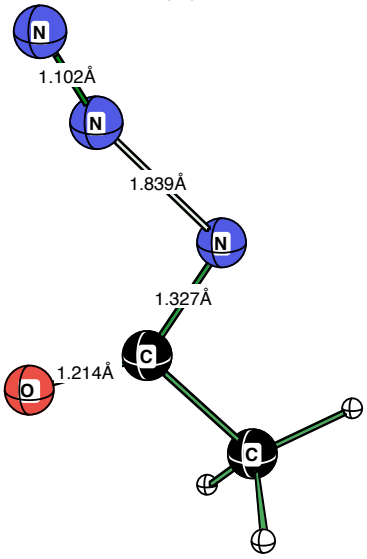
---



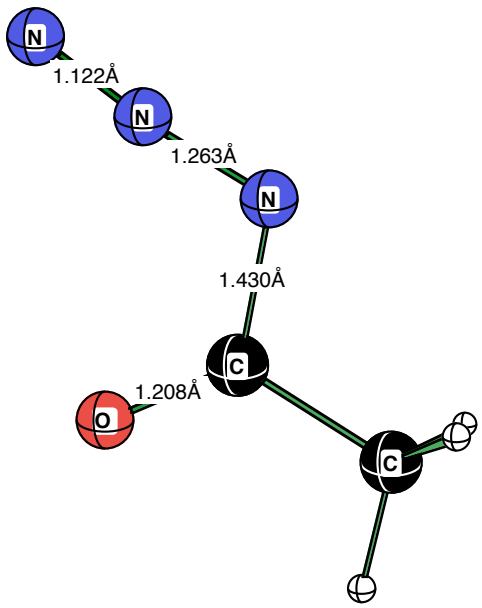

FOpt\RCCSD-FC\6-311+G(d,p)= -207.5071014

| | | | |
|---|---|---|---|
| 6 | -0.800560 | 0.010359 | -1.535696 |
| 1 | -1.809241 | 0.349247 | -1.777568 |
| 6 | 0.341652 | -0.008397 | 0.636431 |
| 8 | 1.157348 | -0.161718 | 1.463947 |
| 7 | -0.580141 | 0.201625 | -0.113543 |
| 1 | -0.710244 | -1.047286 | -1.803495 |

1 -0.082742 0.593759 -2.121247
\SP\RCCSD(T)-FC\6-311+G(d,p)= -207.5362827 a.u.




Transition state for rearrangement of acetylazide: geometry is ccsd 2YES +6cyc
SP\RCCSD(T)-FC\6-311+G(d,p)
Charge = 0 Multiplicity = 1
C 0.1549317575,0.0006585259,-0.7953782986
O 1.3579795309,0.0031723244,-0.6301428948
N -0.9160979026,-0.0023177101,-0.0123634257
C -0.540981894,0.0000238949,-2.1925074511
H -1.6333522426,0.0000168148,-2.1606641599
H -0.1843695285,0.8982347487,-2.7020739127
H -0.1843420118,-0.8986275898,-2.7012898214
N -0.1270629682,-0.0015357799,1.6486837357
N 0.1080934929,-0.0003032377,2.7254633402
CCSD=-316.6771052\CCSD(T)=-316.7235659




ground state for acetylazide: FOpt\RCCSD-FC\6-311+G(d,p)
CCSD=-316.71654
Charge = 0 Multiplicity = 1
C -0.5006452471,0.0000032685,2.1211261126
C 0.1592603145,-0.000460774,0.7644314005
O 1.3503302077,-0.0013130618,0.5652648433
N -0.8169633748,0.0004004747,-0.2798405936
N -0.2692023309,0.0005657129,-1.4176548087
N 0.1224763883,0.0008066768,-2.4694427895
H 0.2675931621,-0.0033124723,2.8955320432
H -1.1410536416,-0.8826446097,2.217797917
H -1.1350463652,0.8867965586,2.2197735577
\CCSD=-316.71654\CCSD(T)=-316.7654787

**Figure 4.** Cyclopropyl acyl azide *syn* and *anti* minima (**5a** and **5b**) and *syn*-**TS-5** ($\Delta E^{\ddagger}$ =29.3 kcal/mol) optimized at the B3LYP/6-311+G(d,p) level of theory.

RB3LYP/6-311+G(d,p) **5a E =-394.9419708**
Zero-point correction= 0.094543 (Hartree/Particle)
Thermal correction to Energy= 0.101955
Thermal correction to Enthalpy= 0.102899
Thermal correction to Gibbs Free Energy= 0.062083
Sum of electronic and zero-point Energies= -394.847428
Sum of electronic and thermal Energies= -394.840016
Sum of electronic and thermal Enthalpies= -394.839072
Sum of electronic and thermal Free Energies= -394.879887

Charge = 0 Multiplicity = 1
C,0,0.0501196739,0.8708625393,-2.3818069049
C,0,0.4058253297,0.9904281906,-0.9043634077
C,0,1.46402243,0.6797160695,-1.9566656026
H,0,-0.5126354786,-0.009618906,-2.6649233422
H,0,-0.2291255358,1.7885563715,-2.8840336651
H,0,0.4050978178,1.9758024994,-0.4589106295
H,0,2.1847359353,1.4622251067,-2.1582176392
H,0,1.8552804096,-0.3297387477,-1.9529232969
C,0,-0.0115710902,-0.11122043,-0.011527052
O,0,-0.0780347659,-1.2801178921,-0.3160445389
N,0,-0.3385416647,0.3803687565,1.2969241667
N,0,-0.699850157,-0.492768688,2.1059670017
N,0,-1.0372443328,-1.2054574118,2.9076149297

Figure 4. RB3LYP/6-311+G(d,p) **5b E= -394.940283**
Zero-point correction= 0.094584 (Hartree/Particle)
Thermal correction to Energy= 0.101984
Thermal correction to Enthalpy= 0.102928
Thermal correction to Gibbs Free Energy= 0.062158
Sum of electronic and zero-point Energies= -394.845699
Sum of electronic and thermal Energies= -394.838300
Sum of electronic and thermal Enthalpies= -394.837355
Sum of electronic and thermal Free Energies= -394.878125
Charge = 0 Multiplicity = 1
C,0,-0.6846338568,-0.7452944281,-2.1018200521
C,0,-1.248342485,-0.0000026439,-0.8978434119
C,0,-0.6846440746,0.7452937618,-2.10182191
H,0,0.262512911,-1.2507528139,-1.9661737794
H,0,-1.4060499623,-1.2707880743,-2.7151082564
H,0,-2.3226899142,-0.0000098537,-0.7699214183
H,0,-1.4060673712,1.270776006,-2.7151114275
H,0,0.2624957159,1.250765518,-1.9661767591
C,0,-0.5413905335,0.0000038925,0.4006837285
O,0,-1.0857192247,-0.0000044281,1.4788470493
N,0,0.8917166802,0.0000044054,0.2483011208
N,0,1.5295488962,0.0000020232,1.3123523255
N,0,2.1858227262,-0.0000005501,2.2259929993

**Figure 5**. Cyclopropyl and cyclopropenyl acyl azides (*syn-syn* and syn-*anti* minima (**6a** and **6b**) and the corresponding transition structures (*syn-syn*-**TS-6** (a second-order saddle point) and syn-*anti*-**TS-6**) optimized at the B3LYP/6-311+G(d,p) level of theory.

Figure 5. RB3LYP/6-311+G(d,p) *syn-syn* **6a E=-393.6658531**
Zero-point correction= 0.069220 (Hartree/Particle)
Thermal correction to Energy= 0.076563
Thermal correction to Enthalpy= 0.077507
Thermal correction to Gibbs Free Energy= 0.036914
Sum of electronic and zero-point Energies= -393.596633
Sum of electronic and thermal Energies= -393.589290
Sum of electronic and thermal Enthalpies= -393.588346
Sum of electronic and thermal Free Energies= -393.628939
Charge = 0 Multiplicity = 1
C,0,-1.5354869687,-0.6420640391,1.7220097686
C,0,-0.1680692972,-0.0000624165,1.6035058399
C,0,-1.5355954228,0.6417148438,1.721968216
H,0,0.5139322664,0.0000191014,2.4515570316
C,0,0.5846798419,-0.0000470475,0.3157113539
O,0,1.7889254568,0.0000683159,0.2319254099
N,0,-0.2874893872,-0.0000372058,-0.8297101667
N,0,0.2933877612,0.0000724913,-1.9258480031
N,0,0.7338808733,0.0003387557,-2.9614677288
H,0,-2.0386128383,1.5910527484,1.7664963489
H,0,-2.0383467329,-1.5914847086,1.7665535595

Figure 5. RB3LYP/6-311+G(d,p) **6b E=-393.6662627**
Zero-point correction= 0.069156 (Hartree/Particle)
Thermal correction to Energy= 0.076535
Thermal correction to Enthalpy= 0.077479
Thermal correction to Gibbs Free Energy= 0.036753
Sum of electronic and zero-point Energies= -393.597107
Sum of electronic and thermal Energies= -393.589728
Sum of electronic and thermal Enthalpies= -393.588784
Sum of electronic and thermal Free Energies= -393.629510
Charge = 0 Multiplicity = 1
C,0,2.2434943545,-1.3651443005,0.0989222006
C,0,0.9364872233,-0.9922958648,-0.5707197781
C,0,2.3601311667,-0.6472533246,-0.9578722367
H,0,0.3758854256,-1.7334635542,-1.1360743828
C,0,0.0899543771,0.0664944548,0.0550963363
O,0,0.4851150745,0.9894558366,0.7256815686
N,0,-1.2979927517,-0.1548153023,-0.2484205441

N,0,-2.0781644793,0.6833395762,0.234840168
N,0,-2.8575328634,1.3916996463,0.6300198697
H,0,2.944108963,-0.1060591404,-1.6804552858
H,0,2.6545129463,-1.8884972285,0.9434415314

Figure 5. RB3LYP/6-311+G(d,p) *syn-syn*-TS-**6 E= -393.615401**
**Im. Freq= 561.5487i cm$^{-1}$; 20.5890i cm$^{-1}$**
Zero-point correction= 0.064525 (Hartree/Particle)
Thermal correction to Energy= 0.071907
Thermal correction to Enthalpy= 0.072852
Thermal correction to Gibbs Free Energy= 0.032112
Sum of electronic and zero-point Energies= -393.550876
Sum of electronic and thermal Energies= -393.543494
Sum of electronic and thermal Enthalpies= -393.542549
Sum of electronic and thermal Free Energies= -393.583289
Charge = 0 Multiplicity = 1
C,0,-2.5604407371,0.0191848189,-0.647521493
C,0,-1.4284745091,-0.7007854761,0.0000697333
C,0,-2.5606290846,0.0194350867,0.6471034718
H,0,-1.3488553408,-1.7809251713,0.0002663927
C,0,-0.0415202831,0.14006517,0.0003721488
O,0,-0.0496037439,1.3560925938,0.0011940119
N,0,0.8212160498,-0.8277833815,-0.0004965332
N,0,2.4185283771,-0.0243477817,-0.0002467174
N,0,3.5159786068,-0.0848631456,-0.0005899552
H,0,-2.9991959343,0.312171618,1.5844975638
H,0,-2.9987923259,0.311575367,-1.585126777

Figure 5. RB3LYP/6-311+G(d,p) *syn-anti*-TS-**6 E=-393.6165156**
**Im. Freq= 606.7141i cm$^{-1}$**
Zero-point correction= 0.064730 (Hartree/Particle)
Thermal correction to Energy= 0.072806
Thermal correction to Enthalpy= 0.073750
Thermal correction to Gibbs Free Energy= 0.031020
Sum of electronic and zero-point Energies= -393.551786
Sum of electronic and thermal Energies= -393.543710
Sum of electronic and thermal Enthalpies= -393.542766
Sum of electronic and thermal Free Energies= -393.585495
C,0,-1.3269209789,0.155637066,-2.1024906908
C,0,-0.5798890197,0.9820365477,-1.1056610754
C,0,-0.2027010385,0.6435747688,-2.5128862958
H,0,-0.9256923587,1.9729647779,-0.8145180449
C,0,0.3569910075,0.3754220201,0.0219136606
O,0,1.5568474094,0.5740529303,0.0634006059
N,0,-0.5336916228,-0.2688613974,0.7284706776
N,0,0.315861942,-0.9799925363,2.0348015742

N,0,0.3084898528,-1.5860702747,2.9538943278
H,0,-2.2185091488,-0.4238270244,-2.2665316697
H,0,0.5699212058,0.7628858481,-3.2515747815

**Figure 6.** Structures of **1, 3** minima and their corresponding transition structures, **TS-1 and TS-3**, optimized at the B3LYP/6-311+G(d,p) level of theory.

Figure 6. RB3LYP/6-311+G(d,p) **3 E=** -622.8790512
Zero-point correction= 0.136880 (Hartree/Particle)
Thermal correction to Energy= 0.148782
Thermal correction to Enthalpy= 0.149726
Thermal correction to Gibbs Free Energy= 0.097360
Sum of electronic and zero-point Energies= -622.742171
Sum of electronic and thermal Energies= -622.730270
Sum of electronic and thermal Enthalpies= -622.729325
Sum of electronic and thermal Free Energies= -622.781691

Charge = 0 Multiplicity = 1
C,0,-2.2503358503,-0.6237668688,0.628637202
C,0,-0.8923540655,0.0559976507,0.4403276791
C,0,-2.1024669883,0.8127044168,0.9834602603
H,0,-2.7868318754,-0.8742573803,-0.2777432649
H,0,-2.2847573896,-1.3559551435,1.4249088959
H,0,-2.0629592244,1.0780541368,2.032179256
H,0,-2.5161271622,1.5575429918,0.3162147042
C,0,-0.5183595746,0.3252320662,-0.983260649
O,0,-1.1013019624,1.0913373852,-1.7136630736
N,0,0.5530084167,-0.5112355639,-1.4172778367
N,0,0.9024370567,-0.3435325004,-2.598747471
N,0,1.2953850292,-0.2704729565,-3.649681575
C,0,0.1667904726,-0.2633123294,1.4547410486
O,0,-0.00316351,-0.9616051345,2.4255893029
O,0,1.3097755079,0.3938467464,1.1960675925
C,0,2.3915793174,0.1751362052,2.1230593948
H,0,2.107751823,0.5063525952,3.1225868257
H,0,2.6549565607,-0.8826076577,2.1538270653
H,0,3.2205535979,0.7669787821,1.7422345073

Figure 6. RB3LYP/6-311+G(d,p) TS-**3 E=** -622.8302935
($\nu_i$= 534.8i $cm^{-1}$ )
Zero-point correction= 0.132401 (Hartree/Particle)
Thermal correction to Energy= 0.145058

Thermal correction to Enthalpy= 0.146002
Thermal correction to Gibbs Free Energy= 0.091895
Sum of electronic and zero-point Energies= -622.697893
Sum of electronic and thermal Energies= -622.685235
Sum of electronic and thermal Enthalpies= -622.684291
Sum of electronic and thermal Free Energies= -622.738398
C,0,-0.5669100959,2.0498778719,-0.9693780739
C,0,-0.4616188087,0.8409913206,-0.0246282084
C,0,-0.8015432213,2.2433673462,0.4808606422
H,0,0.3572440258,2.4030047165,-1.4041932194
H,0,-1.4260486964,2.0353268305,-1.6279055732
H,0,-1.8213371151,2.3581508796,0.8266913101
H,0,-0.0407892746,2.7245587326,1.0820327148
C,0,0.8965412753,0.2733272335,0.5262961879
O,0,1.1375131391,0.0756982366,1.6985030708
N,0,1.4984850383,0.149847342,-0.6307612925
N,0,3.0946231934,-0.53310407,-0.2341799582
N,0,4.0777347723,-0.946712365,-0.4972851622
C,0,-1.5881967793,-0.1431271366,-0.1067593593
O,0,-2.7411254079,0.1801545219,-0.2754084032
O,0,-1.1703523551,-1.4085097752,0.018955822
C,0,-2.1925056919,-2.4236800737,-0.0317677142
H,0,-2.9168722431,-2.2703849415,0.768657911
H,0,-2.704185008,-2.3980414915,-0.9944581111
H,0,-1.6667957942,-3.3661143137,0.1006150966

Figure 6. RB3LYP/6-311+G(d,p) TS-**1** **E=** -621.5594629 ($\nu_i$= 589.0i $cm^{-1}$ )
Zero-point correction= 0.107027 (Hartree/Particle)
Thermal correction to Energy= 0.119638
Thermal correction to Enthalpy= 0.120582
Thermal correction to Gibbs Free Energy= 0.066451
Sum of electronic and zero-point Energies= -621.452436
Sum of electronic and thermal Energies= -621.439825
Sum of electronic and thermal Enthalpies= -621.438881
Sum of electronic and thermal Free Energies= -621.493012
Charge = 0 Multiplicity = 1
C,0,-2.1729441343,-0.8287172954,0.5942586448
C,0,-0.9037718705,-0.0312739686,0.4954871666
C,0,-2.2999498122,0.4305906074,0.8143913694
C,0,-0.3404122511,0.5146586803,-0.8932441304
O,0,-0.2598212825,1.6977418445,-1.1548494783
N,0,-0.1099467718,-0.6302994995,-1.4756699925
N,0,0.5098917123,-0.2431211598,-3.0478338966
N,0,0.9336858371,-0.562356752,-4.0116681052
C,0,0.1112867138,-0.1425939389,1.6078340596

O,0,-0.1853009997,-0.3866708586,2.7524092806
O,0,1.3625533304,0.062353438,1.1763922218
C,0,2.3990061303,-0.0048183249,2.1755387168
H,0,2.2268939605,0.7439249963,2.9494030363
H,0,2.423031257,-0.9961085501,2.6295629941
H,0,3.3251913753,0.197866396,1.6432793069
H,0,-2.8553468231,1.3217650161,1.0433616632
H,0,-2.553922253,-1.8314759292,0.523385805

Figure 6. RB3LYP/6-311+G(d,p) **1 E=** -621.6038235
Zero-point correction= 0.111337 (Hartree/Particle)
Thermal correction to Energy= 0.123267
Thermal correction to Enthalpy= 0.124211
Thermal correction to Gibbs Free Energy= 0.071553
Sum of electronic and zero-point Energies= -621.492487
Sum of electronic and thermal Energies= -621.480557
Sum of electronic and thermal Enthalpies= -621.479612
Sum of electronic and thermal Free Energies= -621.532270
Charge = 0 Multiplicity = 1
C,0,-2.3378815995,-0.4987857395,0.7087290537
C,0,-0.9559097991,0.0693361003,0.4679723285
C,0,-2.2075378837,0.7496637873,0.9751635288
C,0,-0.5517906115,0.3534301567,-0.957471108
O,0,-1.0594393324,1.1981435713,-1.6533272955
N,0,0.4501973477,-0.5557747283,-1.4170680687
N,0,0.8311017266,-0.371320076,-2.5860161269
N,0,1.2409979342,-0.2855168712,-3.6296875049
C,0,0.1222203563,-0.2723471823,1.4706749528
O,0,-0.0375929906,-1.0023709871,2.4177205673
O,0,1.2639935607,0.3905337424,1.2133664671
C,0,2.3612280616,0.1402405275,2.1135753165
H,0,2.0934787618,0.4345510033,3.1290211134
H,0,2.6249971539,-0.9178987914,2.1021095301
H,0,3.1844871521,0.745750245,1.7417564694
H,0,-2.575041842,1.697287266,1.3245479433
H,0,-2.9016613315,-1.4110845068,0.6380245014

**1 reactant** mpw1pw91/6-31g(d) **E =-621.2673054**
Zero-point correction= 0.114014 (Hartree/Particle)
Thermal correction to Energy= 0.125815
Thermal correction to Enthalpy= 0.126759
Thermal correction to Gibbs Free Energy= 0.074533
Sum of electronic and zero-point Energies= -621.153292
Sum of electronic and thermal Energies= -621.141490
Sum of electronic and thermal Enthalpies= -621.140546
Sum of electronic and thermal Free Energies= -621.192772

C,0,-2.3105396227,-0.5193306089,0.7175311188
C,0,-0.9428037872,0.0628001467,0.4673895184
C,0,-2.195276601,0.7366112831,0.9631687255
C,0,-0.5551461356,0.334716879,-0.9601756691
O,0,-1.1247947376,1.1270770927,-1.6721596291
N,0,0.4976069997,-0.5104767901,-1.4037961287
N,0,0.8369151487,-0.3302618959,-2.5834307226
N,0,1.2189134973,-0.2437490513,-3.6407984673
C,0,0.1296462443,-0.2561098576,1.4766867736
O,0,-0.0541781287,-0.9290812097,2.4623502842
O,0,1.2865983046,0.3513671665,1.1863233114
C,0,2.3481702914,0.1066741155,2.1082168965
H,0,2.0805594844,0.4662886833,3.1036408434
H,0,2.5669632149,-0.9612659839,2.1635106134
H,0,3.2058112528,0.6536651375,1.720658333
H,0,-2.5713395941,1.6881031863,1.2976394824
H,0,-2.8613497195,-1.4424530046,0.6617120426

**TS-1** mpw1pw91/6-31g(d) **E =-621.2135792**
$\nu_i$=629.847icm$^{-1}$
Zero-point correction= 0.109434 (Hartree/Particle)
Thermal correction to Energy= 0.121974
Thermal correction to Enthalpy= 0.122918
Thermal correction to Gibbs Free Energy= 0.069020
Sum of electronic and zero-point Energies= -621.104145
Sum of electronic and thermal Energies= -621.091606
Sum of electronic and thermal Enthalpies= -621.090661
Sum of electronic and thermal Free Energies= -621.144559
Charge = 0 Multiplicity = 1
C,0,-2.1515431332,-0.8272299203,0.5774280854
C,0,-0.8921955729,-0.0260714102,0.4847355792
C,0,-2.2814962524,0.4307505824,0.8139434689
C,0,-0.3404450946,0.5623238126,-0.8896748164
O,0,-0.2768597466,1.7470915625,-1.1387825687
N,0,-0.1136008841,-0.5909972881,-1.4410260021
N,0,0.5048582884,-0.2562557092,-3.0309861665
N,0,0.9077791333,-0.6591895796,-3.978580126
C,0,0.1230633513,-0.1516209697,1.5878718565
O,0,-0.1694479461,-0.4312478785,2.72602201
O,0,1.3650199695,0.0833888153,1.1608699849
C,0,2.3781441378,-0.0014221994,2.1629791812
H,0,2.1879154401,0.7201525449,2.9595010527
H,0,2.4078277955,-1.005104087,2.591056448
H,0,3.3126345229,0.2266503,1.6539258349

H,0,-2.8375205775,1.321821923,1.0495410736
H,0,-2.5269757749,-1.8326620092,0.4915461149

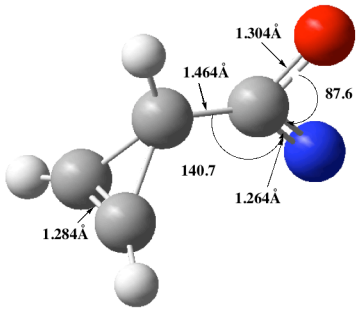
**3 reactant** mpw1pw91/6-31g(d) **E=-622.5467333**
Zero-point correction= 0.140168 (Hartree/Particle)
Thermal correction to Energy= 0.151889
Thermal correction to Enthalpy= 0.152833
Thermal correction to Gibbs Free Energy= 0.100971
Sum of electronic and zero-point Energies= -622.406565
Sum of electronic and thermal Energies= -622.394844
Sum of electronic and thermal Enthalpies= -622.393900
Sum of electronic and thermal Free Energies= -622.445762
C,0,-2.2131501096,-0.6457068577,0.6419915026
C,0,-0.8699775691,0.0481122743,0.4380057614
C,0,-2.0886776794,0.7904706422,0.9678020431
H,0,-2.7461383807,-0.9234271126,-0.2602529072
H,0,-2.2288691191,-1.3631211372,1.4543413393
H,0,-2.0480340656,1.0766562668,2.0124451062
H,0,-2.5124520406,1.5160832488,0.2832924353
C,0,-0.5245236931,0.3001215444,-0.9898986743
O,0,-1.1902986601,0.9815154594,-1.7367690781
N,0,0.6108197437,-0.4374136936,-1.4122497339
N,0,0.9053463754,-0.2787544317,-2.6074070783
N,0,1.2616846442,-0.206774755,-3.6744801175
C,0,0.1759081601,-0.2408695925,1.4667402305
O,0,-0.0364455075,-0.8485581026,2.4908907813
O,0,1.3480329262,0.3272824414,1.167737861
C,0,2.3836463461,0.1213960695,2.1286183507
H,0,2.1019323271,0.5503328939,3.0920580574
H,0,2.5790237642,-0.94462325,2.2572428618
H,0,3.2599193725,0.6256363867,1.7253998174

**TS-3** mpw1pw91/6-31g(d) **E** = -622.4882168
$v_i$= 585.9788i $cm^{-1}$
Zero-point correction= 0.135349 (Hartree/Particle)
Thermal correction to Energy= 0.147900
Thermal correction to Enthalpy= 0.148845
Thermal correction to Gibbs Free Energy= 0.095002
Sum of electronic and zero-point Energies= -622.352868
Sum of electronic and thermal Energies= -622.340316
Sum of electronic and thermal Enthalpies= -622.339372
Sum of electronic and thermal Free Energies= -622.393215
Charge = 0 Multiplicity = 1
C,0,-0.5504066817,2.0431984427,-0.9450372712
C,0,-0.4475867185,0.8315961383,-0.0178742421
C,0,-0.8178378029,2.2186806414,0.494031538

H,0,0.380149153,2.4112630453,-1.3580792234
H,0,-1.3965850316,2.0194310883,-1.6225612159
H,0,-1.849187111,2.3083702257,0.8179672379
H,0,-0.0786644735,2.7015887249,1.1229919345
C,0,0.9006527062,0.2863544396,0.5723005659
O,0,1.1519231178,0.1394299675,1.7477582532
N,0,1.4501697877,0.1284343173,-0.5987048352
N,0,3.0641486067,-0.5501543875,-0.261020418
N,0,4.0330707992,-0.9510856821,-0.6065236937
C,0,-1.5629122642,-0.1536919368,-0.1261814722
O,0,-2.706759097,0.1645549289,-0.3612370658
O,0,-1.154225048,-1.408345097,0.0632941742
C,0,-2.1795354075,-2.3994353483,-0.0122702166
H,0,-2.9477770044,-2.211137723,0.7396534694
H,0,-2.6398992192,-2.3969579412,-1.0019231952
H,0,-1.681515438,-3.3482498102,0.1773573166

**Figure 8.** *Anti*-acyl cyclopropene singlet nitrene (**A**) and *syn* and *anti* acyl cyclopropene triplet nitrenes (**B**, **C**)

Figure 8. (A)




MP2/CBSB3
Charge = 0 Multiplicity = 1
C -1.4050483972,-0.6431672144,1.0186090713
C -0.0405041805,-0.0005503907,0.8604939314
C -1.4057826671,0.6403036419,1.0193135203
H 0.6766963956,-0.0007443015,1.6796434757
C 0.5880016057,0.0008323621,-0.461890508
O 1.8395563984,0.0013814337,-0.8282146107
N 0.2840722389,0.0012388651,-1.6884021583
H -1.9017375793,1.592721825,1.0737402928
H -1.8999138417,-1.5962114425,1.0719921352
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.057124 E(Thermal)= 0.062941
E(SCF)= -282.388267 DE(MP2)= -1.042918

DE(CBS)= -0.098480 DE(MP34)= -0.030456
DE(CCSD)= -0.041527 DE(Int)= 0.033173
DE(Empirical)= -0.044994
CBS-QB3 (0 K)= -283.556345 CBS-QB3 Energy= -283.550528
CBS-QB3 Enthalpy= -283.549584 CBS-QB3 Free Energy= -283.585700

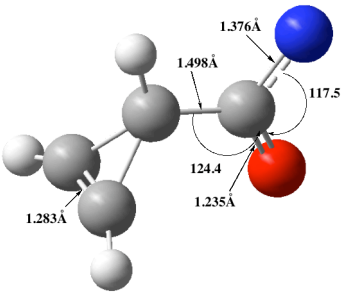



Figure 8. (B)
Charge = 0 Multiplicity = 3
C 0.0394490861,0.6416179178,1.6513455301
C -0.6663033627,-0.0016924768,0.473858031
C 0.0427903376,-0.6411643892,1.6513992801
H -1.7541639599,-0.0044354535,0.4239491439
C 0.0157266787,-0.0000273926,-0.8600612274
O 1.2401108001,0.002404963,-1.017793379
N -0.7694857257,-0.0013050945,-1.9897874712
H 0.3189256152,-1.5904889691,2.0739595635
H 0.3107755848,1.5924184249,2.0737009401
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.056154 E(Thermal)= 0.061965
E(SCF)= -282.467518 DE(MP2)= -0.944650
DE(CBS)= -0.094433 DE(MP34)= -0.047632
DE(CCSD)= -0.040058 DE(Int)= 0.030103
DE(Empirical)= -0.044829
CBS-QB3 (0 K)= -283.552862 CBS-QB3 Energy= -283.547051
CBS-QB3 Enthalpy= -283.546106 CBS-QB3 Free Energy= -283.583489

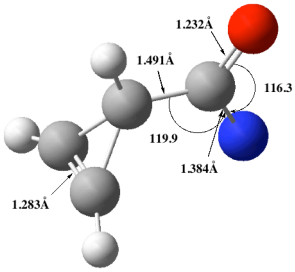



Figure 8. (C)
Charge = 0 Multiplicity = 3
C 0.044701 -0.641594 -1.664233
C -0.651783 -0.000044 -0.475199

| | | | |
|---|---|---|---|
| C | 0.044628 | 0.641614 | -1.664220 |
| H | -1.739334 | -0.000118 | -0.408576 |
| C | -0.006020 | 0.000020 | 0.868253 |
| O | -0.631382 | -0.000010 | 1.929973 |
| N | 1.373791 | 0.000024 | 0.970678 |
| H | 0.292219 | 1.589983 | -2.106779 |
| H | 0.292475 | -1.589920 | -2.106781 |

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.056227 E(Thermal)= 0.062022
E(SCF)= -282.467105 DE(MP2)= -0.945115
DE(CBS)= -0.094410 DE(MP34)= -0.047506
DE(CCSD)= -0.039857 DE(Int)= 0.030149
DE(Empirical)= -0.044749
CBS-QB3 (0 K)= -283.552365 CBS-QB3 Energy= -283.546571
CBS-QB3 Enthalpy= -283.545627 CBS-QB3 Free Energy= -283.582839

**Figure 9.** Minimum (syn-*anti*-**6b**) and transition structure (*syn*-*anti*-**TS6b**) for the Curtius rearrangement and the loss of $N_2$ (TS-**7**) from acyl cyclopropenyl azide at the CBS-QB3 level of theory.

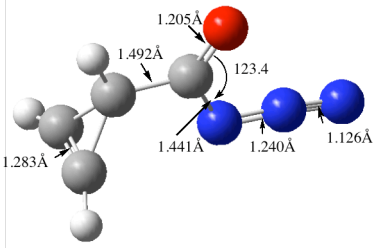



Figure 9. syn-*anti*-**6b** MP2/CBSB3
Charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.534592 | -0.641883 | 1.721116 |
| C | -0.167737 | -0.000044 | 1.603629 |
| C | -1.534706 | 0.641533 | 1.721200 |
| H | 0.515064 | -0.000046 | 2.451192 |
| C | 0.587748 | 0.000118 | 0.316832 |
| O | 1.789860 | 0.000103 | 0.233904 |
| N | -0.286802 | 0.000014 | -0.828746 |
| N | 0.290803 | 0.000031 | -1.925919 |
| N | 0.730187 | 0.000145 | -2.962879 |
| H | -2.038914 | 1.590228 | 1.761979 |
| H | -2.038631 | -1.590674 | 1.761748 |

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.068680 E(Thermal)= 0.076063
E(SCF)= -391.390271 DE(MP2)= -1.441333
DE(CBS)= -0.135226 DE(MP34)= -0.015408
DE(CCSD)= -0.051542 DE(Int)= 0.044643

DE(Empirical)= -0.060799
CBS-QB3 (0 K)= -392.981256 CBS-QB3 Energy= -392.973873
CBS-QB3 Enthalpy= -392.972929 CBS-QB3 Free Energy= -393.013611

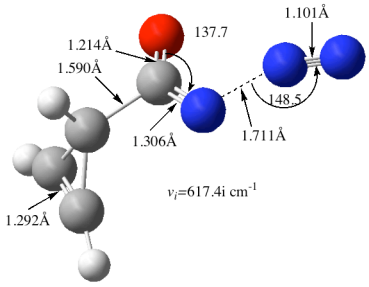



Figure 9. *syn-anti*-**TS6b**
Frequencies -- -617.3645 cm-1 (B3LYP/CBSB7)
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.064200 E(Thermal)= 0.072304
E(SCF)= -391.354984 DE(MP2)= -1.409699
DE(CBS)= -0.132529 DE(MP34)= -0.031998
DE(CCSD)= -0.053248 DE(Int)= 0.044334
DE(Empirical)= -0.060665
CBS-QB3 (0 K)= -392.934588 CBS-QB3 Energy= -392.926485
CBS-QB3 Enthalpy= -392.925541 CBS-QB3 Free Energy= -392.968338
Charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.319859 | 0.152306 | -2.101932 |
| C | -0.589000 | 0.981435 | -1.096203 |
| C | -0.204567 | 0.663744 | -2.506545 |
| H | -0.951388 | 1.963488 | -0.796167 |
| C | 0.366231 | 0.364095 | 0.014278 |
| O | 1.570562 | 0.518955 | 0.010541 |
| N | -0.528709 | -0.237691 | 0.751602 |
| N | 0.315812 | -0.966512 | 2.048243 |
| N | 0.284443 | -1.573143 | 2.967031 |
| H | -2.199072 | -0.443955 | -2.272205 |
| H | 0.568316 | 0.800777 | -3.241663 |

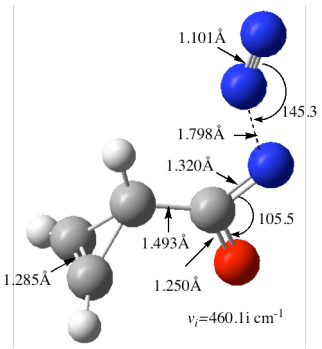


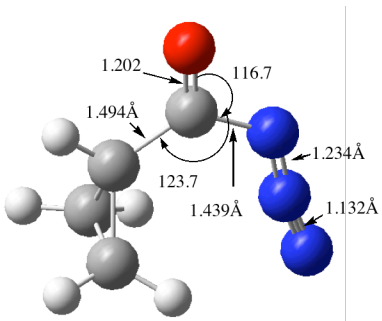

Figure 9. TS-**7**
Frequencies -- -460.1230
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.064411 E(Thermal)= 0.072435

E(SCF)= -391.347892 DE(MP2)= -1.406212
DE(CBS)= -0.132049 DE(MP34)= -0.037014
DE(CCSD)= -0.054929 DE(Int)= 0.044329
DE(Empirical)= -0.060629
CBS-QB3 (0 K)= -392.929984 CBS-QB3 Energy= -392.921960
CBS-QB3 Enthalpy= -392.921016 CBS-QB3 Free Energy= -392.963268
Charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -2.193294 | -0.786232 | -0.642252 |
| C | -0.829370 | -0.679022 | -0.000084 |
| C | -2.193173 | -0.786495 | 0.642297 |
| H | -0.153391 | -1.531404 | -0.000321 |
| C | -0.197982 | 0.673365 | 0.000131 |
| O | -0.839729 | 1.745549 | 0.000391 |
| N | 1.073981 | 1.024435 | 0.000099 |
| N | 2.126668 | -0.433487 | -0.000265 |
| N | 3.165142 | -0.800122 | -0.000411 |
| H | -2.698717 | -0.804032 | 1.590799 |
| H | -2.699016 | -0.803381 | -1.590666 |

**Figure 10**. *Anti-anti* and *anti-syn*-acyl cyclopropyl azides **8** (*anti-anti*-**8** and *anti-syn*-**8**) and the *anti-syn*-TS-**8** for Curtius rearrangent and *anti-syn*-TS-**8a** for loss of N2 to produce cyclopropyl acyl nitrene.

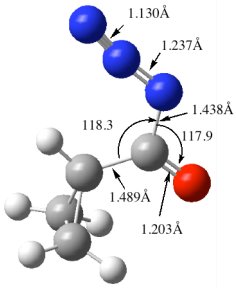
*anti-anti*-8




Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.093679 E(Thermal)= 0.101096
E(SCF)= -392.602599 DE(MP2)= -1.477300
DE(CBS)= -0.138759 DE(MP34)= -0.022297
DE(CCSD)= -0.049802 DE(Int)= 0.045942
DE(Empirical)= -0.064018
CBS-QB3 (0 K)= -394.215153 CBS-QB3 Energy= -394.207736
CBS-QB3 Enthalpy= -394.206792 CBS-QB3 Free Energy= -394.247448
Charge = 0 Multiplicity = 1
C -0.6284400325,1.6062335692,-0.7476856227
C -1.2196512011,0.4213809693,-0.0000130498
C -0.627860187,1.6059353611,0.747734102
H -2.3000752338,0.3576539085,0.0004349122

C -0.660572079,-0.9643174774,-0.0003661219
O -1.3806120814,-1.9262646244,0.0005815484
N 0.7561952024,-1.2182181229,-0.0007828589
N 1.6111749895,-0.3283334561,-0.0001331052
N 2.5197940428,0.3466730928,0.0004539954
H -1.3363497207,2.2357379021,1.270590777
H -1.3373256145,2.2362665508,-1.2697285312
H 0.3133297162,1.4823693377,-1.2650568053
H 0.3143088585,1.4818441655,1.2643251951

*anti-syn*-8




Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.093677 E(Thermal)= 0.101130
E(SCF)= -392.612860 DE(MP2)= -1.473705
DE(CBS)= -0.138707 DE(MP34)= -0.023042
DE(CCSD)= -0.049569 DE(Int)= 0.045842
DE(Empirical)= -0.064084
CBS-QB3 (0 K)= -394.222449 CBS-QB3 Energy= -394.214996
CBS-QB3 Enthalpy= -394.214052 CBS-QB3 Free Energy= -394.255322
Charge = 0 Multiplicity = 1
C -0.6952705089,-0.7438673292,-2.0226739459
C -0.5707073876,-0.0001927446,-0.6991886373
C -0.6952095829,0.7438994863,-2.0224495134
H -1.4390509913,-0.0002473194,-0.0533849437
C 0.7723731503,-0.000367454,-0.0568388267
O 1.8074022073,0.0002375911,-0.6691957275
N 0.8402188833,0.0000295701,1.3796573785
N -0.2061733375,0.0001104574,2.0396147443
N -1.0742428853,0.0002360648,2.7633483105
H -1.6249712164,1.2707570254,-2.1965699332
H -1.6250767682,-1.2705963677,-2.196943066
H 0.2017492655,-1.2434391601,-2.3650972904
H 0.2018521718,1.2434961797,-2.3647275491

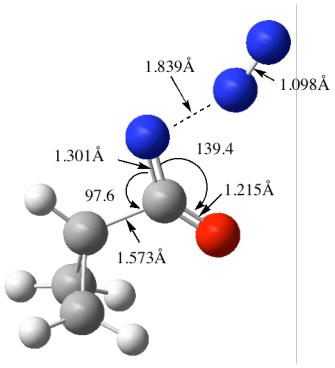
**8(*syn*C-N, *syn*C–C)**

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.093766 E(Thermal)= 0.101210
E(SCF)= -392.625269 DE(MP2)= -1.467565
DE(CBS)= -0.138428 DE(MP34)= -0.025139
DE(CCSD)= -0.048693 DE(Int)= 0.045657
DE(Empirical)= -0.064212
CBS-QB3 (0 K)= -394.229883 CBS-QB3 Energy= -394.222439
CBS-QB3 Enthalpy= -394.221495 CBS-QB3 Free Energy= -394.262364
Charge = 0 Multiplicity = 1
C 2.0602096718,0.7436281812,-2.1322563825
C 2.0068817873,-0.0004745043,-0.8042828418
C 2.0600161705,-0.7449092487,-2.1320785524
H 2.8907512457,-0.0005163384,-0.1813448143
C 0.7161781497,-0.0002173771,-0.0817236928
O -0.3769169609,-0.0001787253,-0.5968408035
N 0.9195407196,-0.0001283017,1.339030847
N -0.1234228027,0.000036413,2.0163761267
N -1.0060182934,0.0001927795,2.7137602376
H 2.9795477097,-1.2717093036,-2.3539104068
H 2.9798782917,1.2701364865,-2.354212691
H 1.1477450573,1.2446917583,-2.4294315518
H 1.1474212538,-1.2458068195,-2.4291334743

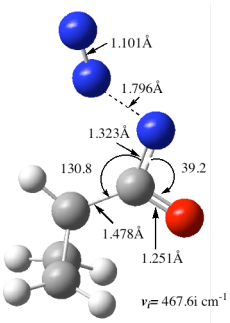
**8(*syn*C-N, *anti*C–C)**

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.093795 E(Thermal)= 0.101232
E(SCF)= -392.623063 DE(MP2)= -1.468636
DE(CBS)= -0.138434 DE(MP34)= -0.025058
DE(CCSD)= -0.048667 DE(Int)= 0.045652
DE(Empirical)= -0.064201
CBS-QB3 (0 K)= -394.228612 CBS-QB3 Energy= -394.221174
CBS-QB3 Enthalpy= -394.220230 CBS-QB3 Free Energy= -394.261058
Charge = 0 Multiplicity = 1
C 2.0455031854,0.7397500851,-2.1651818271
C 1.99056613,0.0017857147,-0.8339932467
C 2.0692380694,-0.7503707254,-2.1560203562
H 2.877593672,0.0197006567,-0.2148962302
C 0.7561316835,-0.0129765268,-0.0186523662
O 0.7275436606,-0.0063437523,1.186453515
N -0.43605749,-0.0366848562,-0.8318800857
N -1.5012204158,-0.0499760282,-0.1973139963
N -2.511064764,-0.0633319544,0.2995181141
H 3.0017461575,-1.2623259723,-2.3583954868
H 2.9612701982,1.2786045818,-2.3740772362
H 1.1366301082,1.2280479381,-2.491220675

H 1.1764358051,-1.2713401608,-2.4758401226




*anti-syn*-TS-**8** for Curtius rearrangent
Frequencies -- -478.5237
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.089158 E(Thermal)= 0.097377
E(SCF)= -392.595387 DE(MP2)= -1.428891
DE(CBS)= -0.135317 DE(MP34)= -0.044313
DE(CCSD)= -0.050234 DE(Int)= 0.045286
DE(Empirical)= -0.064139
CBS-QB3 (0 K)= -394.183837 CBS-QB3 Energy= -394.175618
CBS-QB3 Enthalpy= -394.174674 CBS-QB3 Free Energy= -394.217528
C 0.000542434,-0.7576377924,-2.4400886159
C -0.6591657952,-0.0003070047,-1.3212121002
C -0.0004618084,0.7580453772,-2.4399881809
H -1.7387775941,-0.0010218166,-1.2703273324
C 0.1667447054,0.0001550092,0.0173410073
O 1.3818003917,0.0009613842,0.0455487444
N -0.8405415835,-0.0005677217,0.8410524627
N -0.0467178244,-0.0001453152,2.5002288947
N -0.1001916143,-0.000271153,3.596835102
H 0.9488793719,-1.2306570639,-2.2198744896
H 0.947247105,1.2322947339,-2.2197156675
H -0.6451509195,1.2883463131,-3.1298937937
H -0.6434428688,-1.28870095,-3.130065031




*anti-syn*-TS-**8a** for loss of N2 to produce cyclopropyl acyl nitrene.
Frequencies -- -467.5585
Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.089539 E(Thermal)= 0.097619
E(SCF)= -392.581150 DE(MP2)= -1.433511
DE(CBS)= -0.135350 DE(MP34)= -0.046314
DE(CCSD)= -0.052086 DE(Int)= 0.045369
DE(Empirical)= -0.064033
CBS-QB3 (0 K)= -394.177537 CBS-QB3 Energy= -394.169457
CBS-QB3 Enthalpy= -394.168513 CBS-QB3 Free Energy= -394.211043
Charge = 0 Multiplicity = 1
C -0.722686015,0.7450814589,2.1048102432
C -0.6323858449,0.0000070826,0.7811338998
C -0.722702087,-0.7450539366,2.1048165756
H -1.50433961,0.0000140104,0.1427634476
C 0.6919926496,-0.00001087,0.1255951552
O 1.7893284813,-0.000022307,0.7253712019
N 1.0230130047,-0.0000188958,-1.1557866024
N -0.4378777911,-0.0000041955,-2.1996676505
N -0.8159624168,-0.0000026727,-3.2338509582
H 0.1817054955,-1.2439857231,2.4294456934
H 0.1817320961,1.2439966805,2.429435456
H -1.6470288115,1.272876391,2.3031272252
H -1.647056151,-1.2728273386,2.3031383133