Eur. J. Org. Chem. **2006** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2006 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Formation of 4*H*-Azepine by the Electrophilic Reaction of a 2-Methoxyazepinium Ion and Analysis of the Sigmatropic Isomerization

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Ref. No.: O200600257

2-Methoxy-3*H*-azepine: 4-Nitrobenene (25.0 g, 219 mmol), tri-*n*-butylphosphine (97.4 g, 481 mmol) and 50 ml methanol were heated in an autoclave at 150 °C for 25 hrs. Excess methanol was then removed and the reaction mixture distilled. The fraction from 24 to 26 °C at 4 Torr contained 2-Methoxy-3*H*-azepine (18.3 g, 61%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 2H, 3-H), 3.70 (s, 3H, OMe), 5.30 (td, $^{3}J_{H\text{-}H}$ = 9.0, 6.6 Hz, 1H, 4-H), 6.00 (dd, $^{3}J_{H\text{-}H}$ = 8.1, 5.7 Hz, 1H, 6-H), 6.22 (dd, $^{3}J_{H\text{-}H}$ = 9.0, 5.7 Hz, 1H, 5-H), 6.96 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 1H, 7-H) ppm. Preparation previously reported: M. Masaki, K. Fukui and J. Kita, *Bulletin of the Chemical Society of Japan.,* **1977**, *50*, 2013-2016.

2-Isopropoxy-7-methoxy-2*H*-azepine (1f): NBS (5.41 g, 30.4 mmol) was dropped into a solution of 2-methoxy-3*H*-azepine (3.40 g, 27.8 mmol) and isopropanol (3.50 g, 58.2 mmol) in CH_2Cl_2 (50 ml) stirred at –98 °C under a nitrogen atmosphere. Stirring was continued at –98 °C for 10 hrs before *N*,*N*-dimethylethylamine (10 ml) was introduced then stirred at room temperature for 5 hrs. Volatile components were then removed under reduced pressure then the remaining material was redissolved in CH_2Cl_2, washed once with water then twice with aq K_2CO_3 then dried over $MgSO_4$. Volatile components were then removed under reduced pressure to give **1f** (5.00g, 100%) as a brown oil. Purification of **1f** performed by column chromatography on silica gel eluted by 1:9 v/v AcOEt-hexane gave **1f** as a colorless oil (4.14 g, 82%). Recrystalization from hexane at –5 °C gave colorless prisms, mp 22-23 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.12 (d, $^{3}J_{H\text{-}H}$ = 6.1 Hz, 3H, *i*Pr), 1.26 (d, $^{3}J_{H\text{-}H}$ = 6.4 Hz, 3H, *i*Pr), 3.65 (s, 3H, OMe), 4.01 (tt, $^{3}J_{H\text{-}H}$ = 6.4, 6.1 Hz, 1H, *i*Pr), 4.49 (ddd, $^{3}J_{H\text{-}H}$ = 4.0, 1.8, 0.7 Hz, 1H, 2-H), 5.93 (dddd, $^{3}J_{H\text{-}H}$ = 10.0, 4.0, 1.0, 0.7 Hz, 1H, 3-H), 6.02 (dddd, $^{3}J_{H\text{-}H}$ = 10.0, 5.4, 1.8, 1.0 Hz, 1H, 4-H), 6.45 (ddd, $^{3}J_{H\text{-}H}$ = 11.5, 1.0, 0.7 Hz, 1H, 6-H), 6.70 (dddd, $^{3}J_{H\text{-}H}$ = 11.5, 5.4, 1.0, 0.7 Hz, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.4 (q, *i*Pr), 23.2 (q, *i*Pr), 53.7 (q, OMe), 68.0 (d, *i*Pr), 83.8 (d, C2), 123.7 (d, C4), 125.5 (d, C6), 136.6 (d, C3), 138.0 (d, C5), 158.5 (s, C7) ppm. IR (film) ν_{max} 2974, 1632 (C=N), 1446, 1247, 1201, 1108 cm^{-1}. UV-vis (EtOH) λ_{max} 274 nm (log ε = 3.14). MS (FAB) *m/z* 182 $(M + H)^{+}$. HRMS (FAB) *m/z* found 182.1179, calcd for $C_{10}H_{16}NO_2$ (M + H) 182.1181. Synthetic procedures previously reported: C. E.

J. Cordonier, K. Satake, M. Atarashi, Y. Kawamoto, H. Okamoto and M. Kimura, *Journal of Organic Chemistry*, **2005**, *70*, 3425-3436.

Reaction of 1f with $TiCl_4$ in the presence of benzene: $TiCl_4$ (5.69 g, 30.0 mmol) was added to a solution of **1f** (1.81 g, 10.0 mmol) in benzene (40 ml) cooled in an ice bath. The reaction mixture was then stirred at rt for 15 hrs before quenching with aq K_2CO_3 (8.3 g, 60 mmol). Salts formed were removed by vacuum filtration. The aqueous phase was then separated from the organic phase and washed tree times with CH_2Cl_2. The organic liquors were dried over $MgSO_4$ then volatile components removed. The phenyl substituted compounds were separated from the remaining nonvolatile component by MPLC on ICN 32-63 silica gel at 0 °C eluted by 1:9 v/v AcOEt-hexane. Reaction previously reported: Y. Kubota, K. Satake, H. Okamoto, M. Kimura, *Organic Letters* **2005**, *7*, 5215-5218.

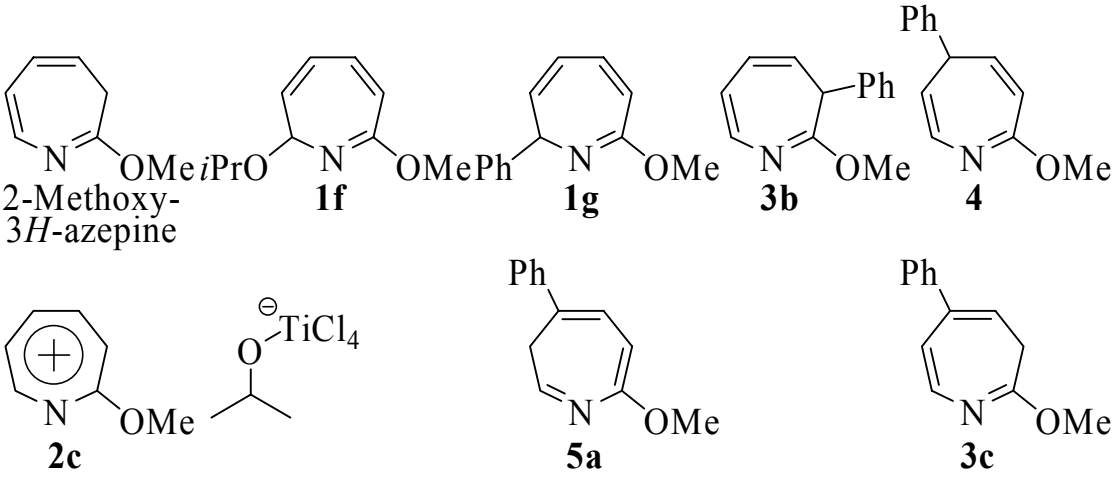
7-Methoxy-2-phenyl-2*H*-azepine (1g): 970 mg, 49% isolated as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OMe), 4.29 (d, $^3J_{H\text{-}H}$ = 5.4 Hz, 1H, 2-H), 5.95 (dd, $^3J_{H\text{-}H}$ = 9.8, 5.4 Hz, 1H, 3-H), 6.24 (dd, $^3J_{H\text{-}H}$ = 9.8, 5.4 Hz, 1H, 4-H), 6.66 (d, $^3J_{H\text{-}H}$ = 11.5 Hz, 1H, 6-H), 6.86 (dd, $^3J_{H\text{-}H}$ = 11.5, 5.4 Hz, 1H, 5-H), 7.33 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, Ph), 7.44 (dd, $^3J_{H\text{-}H}$ = 7.6, 7.1 Hz, 2H, Ph), 7.67 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 53.7 (q, OMe), 58.1 (d, C2), 125.9 (d), 126.2 (d), 126.68 (d), 126.70 (d), 128.3 (d), 137.6 (d), 137.9 (d), 144.3 (s, Ph), 161.7 (s, C7) ppm. IR (film) ν_{max} 3032, 2944, 1632 (C=N), 1444, 1371, 1232, 1197, 1009, 801, 700 cm^{-1}. UV-vis (EtOH) λ_{max} 284 nm (log ε = 3.32). MS (FAB) *m/z* 200 $(M + H)^+$.

2-Methoxy-3-phenyl-3*H*-azepine (3b): 56 mg, 3% isolated as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.31 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 1H, 3-H), 3.68 (s, 3H, OMe), 5.57 (dd, $^3J_{H\text{-}H}$ = 9.0, 6.4 Hz, 1H, 4-H), 6.06 (dd, $^3J_{H\text{-}H}$ = 8.1, 5.9 Hz, 1H, 6-H), 6.36 (dd, $^3J_{H\text{-}H}$ = 9.0, 5.9 Hz, 1H, 5-H), 7.03 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H, 7-H), 7.28-7.32 (m, 3H, Ph), 7.36 (dd, $^3J_{H\text{-}H}$ = 7.8, 7.6 Hz, 2H, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 50.2 (d, C3), 55.3 (q, OMe), 114.6 (d), 121.4 (d), 126.6 (d), 127.0 (d), 128.2 (d), 129.0 (d), 137.0 (d, C7), 137.2 (s, Ph), 150.1 (s, C2) ppm.

7-Methoxy-4-phenyl-4*H*-azepine (4): 854 mg, 43% isolated as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.49-3.52 (m, 1H, 4-H), 3.81 (s, 3H, OMe), 5.10 (ddd, $^3J_{H\text{-}H}$ = 7.1, 5.1, 1.0 Hz, 1H,

3-H), 5.90 (dd, $^3J_{H\text{-}H}$ = 10.0, 1.7 Hz, 1H, 6-H), 6.13 (ddd, $^3J_{H\text{-}H}$ = 10.0, 5.9, 1.0 Hz, 1H, 5-H), 6.66 (dd, $^3J_{H\text{-}H}$ = 7.1, 1.7 Hz, 1H, 2-H), 7.29 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 1H, Ph), 7.32 (dd, $^3J_{H\text{-}H}$ = 7.8, 7.3 Hz, 2H, Ph), 7.37 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 42.8 (d, C4), 52.4 (q, OMe), 116.9 (d), 117.3 (d), 126.8 (d), 127.4 (d), 128.7 (d), 134.2 (d), 142.5 (d), 142.5 (s, Ph), 163.7 (s, C7) ppm. IR (film) ν_{max} 3032, 2946, 1630 (C=N), 1605, 1576, 1437, 1394, 1373, 1241, 1009, 758, 700 cm^{-1}. UV-vis (EtOH) λ_{max} 284 nm (log ε = 3.30). MS (FAB) *m/z* 200 $(M + H)^+$. HRMS (FAB) *m/z* found 200.1065, calcd for $C_{13}H_{14}NO$ (M + H) 200.1075.

2-Methoxyazepinium Isopropyltetrachlorotitanate (2c): A $CDCl_3$ solution of $TiCl_4$ was added to a $CDCl_3$ solution of **1f** in an NMR sample tube then shaken. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.66 (br, 3H, OMe), 8.04 (br, 1H), 8.48 (br, 1H), 8.76 (br, 2H), 9.66 (br, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 60.5 (q, OMe), 132.7 (d), 139.5 (d), 151.3 (d), 152.7 (d), 170.9 (d, C7), 176.9 (s, C2) ppm.



Isomerization of 7-methoxy-4-phenyl-4*H*-azepine (4): A $CDCl_3$ solution of **4** was heated in a sealed NMR sample tube at a specific temperature, *T*, and the ^{1}H NMR spectrum of the mixture measured at intervals over the time required for at least three times the half-life. This procedure was repeated at 5 different temperatures. The time dependent concentrations of each component **4**, **5a** and **3c** at constant temperature, as shown in Figure 1, closely simulate the linear equations for a two consecutive reaction system, a → b → c:

$$a(t)/a_0 = e^{-k_1 t}$$

$$b(t)/a_0 = [k_1/(k_3 - k_1)][e^{-k_1 t} - e^{-k_3 t}]$$

$c(t)/a_0 = 1 - [k_3/(k_3 - k_1)]e^{-k_1 t} + [k_1/(k_3 - k_1)]e^{-k_3 t}$

where a = the concentration of **4**, b = the concentration of **5a**, and c = the concentration of **3c** at time, t, and a_0 = the initial concentration of **4** at t = 0 s,. The first isomerization rate constant, $k_1(T)$, was determined at each temperature by the linear correlation found for the plot $\ln(a/a_0)$ vs t, shown in Figure 2. Given $k_1(T)$, the second isomerization rate constant, $k_3(T)$, was determined at each temperature by fitting the equations for a sequential reaction to the experimental data, shown in Figure 1. In Figure 1, the points are experimental data and the solid lines are the consecutive first order reaction equations given the experimentally estimated rate constants in Table 2 of the article. Figure 3 displays the Arrhenius plot of the isomerization of **4** to **5a**, and **5a** to **3c**. Kinetic parameters were derived from the Arrhenius Parameter, ln A, and slope of the Arrhenius Plot, $-E_a/R$, derived from the Arrhenius plot, ln k vs. T^{-1} shown in figure 3, according to the following equations for a first order reaction:

Arrhenius equation: $\ln k = -E_a/RT + \ln A$

Activation energy, E_a = slope × R

Enthalpy, $\Delta H^{\neq} = E_a - RT$

Entropy, $\Delta S^{\neq} = R\ln(hA/k_bT_{std}) - R$

Gibbs Free Energy, $\Delta G^{\neq} = \Delta H^{\neq} - T_{std} \times \Delta S^{\neq}$

Where R is the ideal gas constant, h is Planck's constant, k_b is the Boltzmann constant, and T_{std} is 298.15K.

Kinetic parameters for the isomerization of:

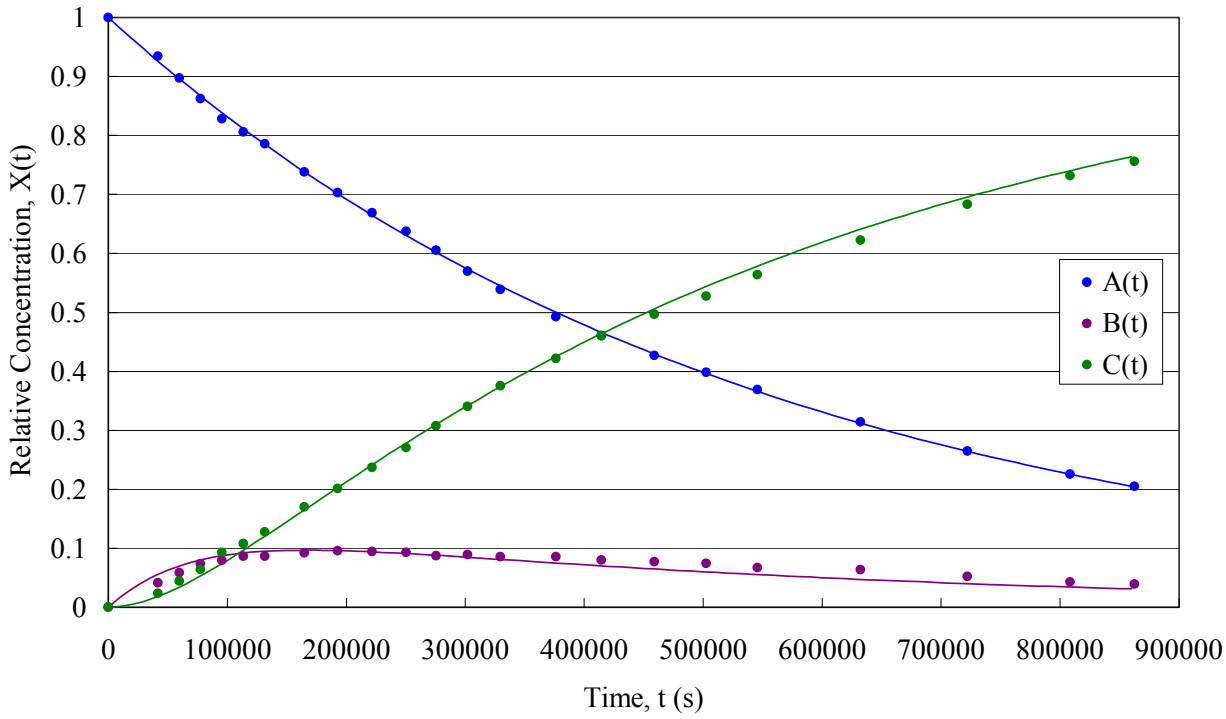
4 → 5a	**5a → 3c**
E_a = 117.0 kJ/mol	E_a = 110.4 kJ/mol
ln A = 21.6	ln A = 21.7
$\Delta H^{\neq}$ = 114.5 kJ/mol	$\Delta H^{\neq}$ = 108.0 kJ/mol
$\Delta S^{\neq}$ = -73.3 J/mol	$\Delta S^{\neq}$ = -73.2 J/mol
$\Delta G^{\neq}$ = 136.3 kJ/mol	$\Delta G^{\neq}$ = 129.8 kJ/mol

7-Methoxy-4-phenyl-3*H*-azepine (5a): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.51 (br, 2H, 3-H), 3.80

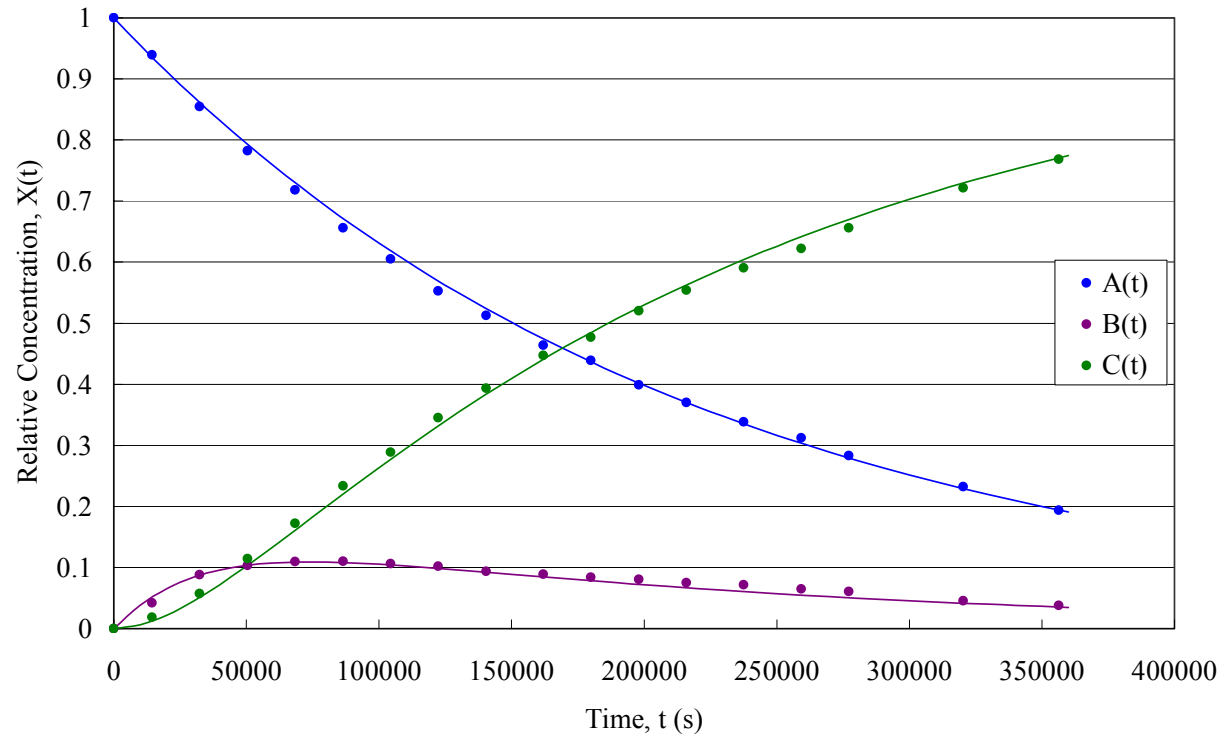
(s, 3H, OMe), 5.83 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, 5-H), 6.50 (t, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, 2-H), 6.78 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, 6-H), 7.30 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 1H, Ph), 7.35 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, Ph), 7.49 (d, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 37.0 (t, C3), 54.4 (q, OMe), 95.6 (d), 115.1 (d), 123.9 (d), 127.0 (d), 127.1 (d), 128.5 (d), 135.2 (s), 139.8 (s), 160.0 (s, C7) ppm. (Not isolated, observed as a component of a mixture.)

2-Methoxy-5-phenyl-3*H*-azepine (3c): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.79 (br, 2H, 3-H), 3.75 (s, 3H, OMe), 5.58 (td, $^{3}J_{H\text{-}H}$ = 7.1, 1.0 Hz, 1H, 4-H), 6.27 (dd, $^{3}J_{H\text{-}H}$ = 8.3, 1.0 Hz, 1H, 6-H), 7.17 (d, $^{3}J_{H\text{-}H}$ = 8.3 Hz, 1H, 7-H), 7.30 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, Ph), 7.35 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H, Ph), 7.42 (d, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 33.2 (t, C3), 54.7 (q, OMe), 113.0 (d), 115.5 (d), 127.4 (d), 127.5 (d), 128.3 (d), 139.0 (d), 139.96 (s), 140.04 (s), 153.1 (s, C2) ppm. IR (film) ν_{max} 3022, 2948, 1626 (C=N), 1537, 1439, 1330, 1245, 1181, 1013, 760, 698 cm^{-1}. UV-vis (EtOH) λ_{max} 239 nm (log ε = 4.30).

(a)


Relative Concentration, X(t)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100000
200000
300000
400000
500000
600000
700000
800000
900000
Time, t (s)
A(t)
B(t)
C(t)

(b)


Relative Concentration, X(t)
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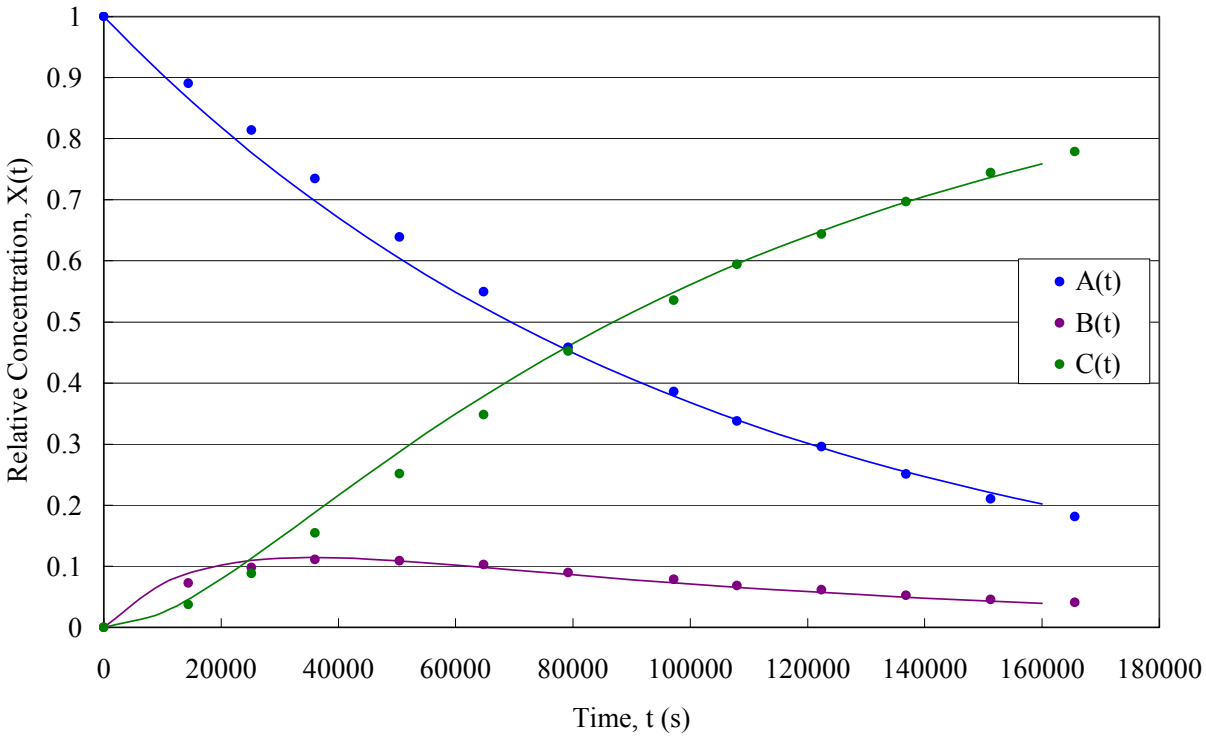
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50000
100000
150000
200000
250000
300000
350000
400000
Time, t (s)
A(t)
B(t)
C(t)

(c)


Relative Concentration, X(t)
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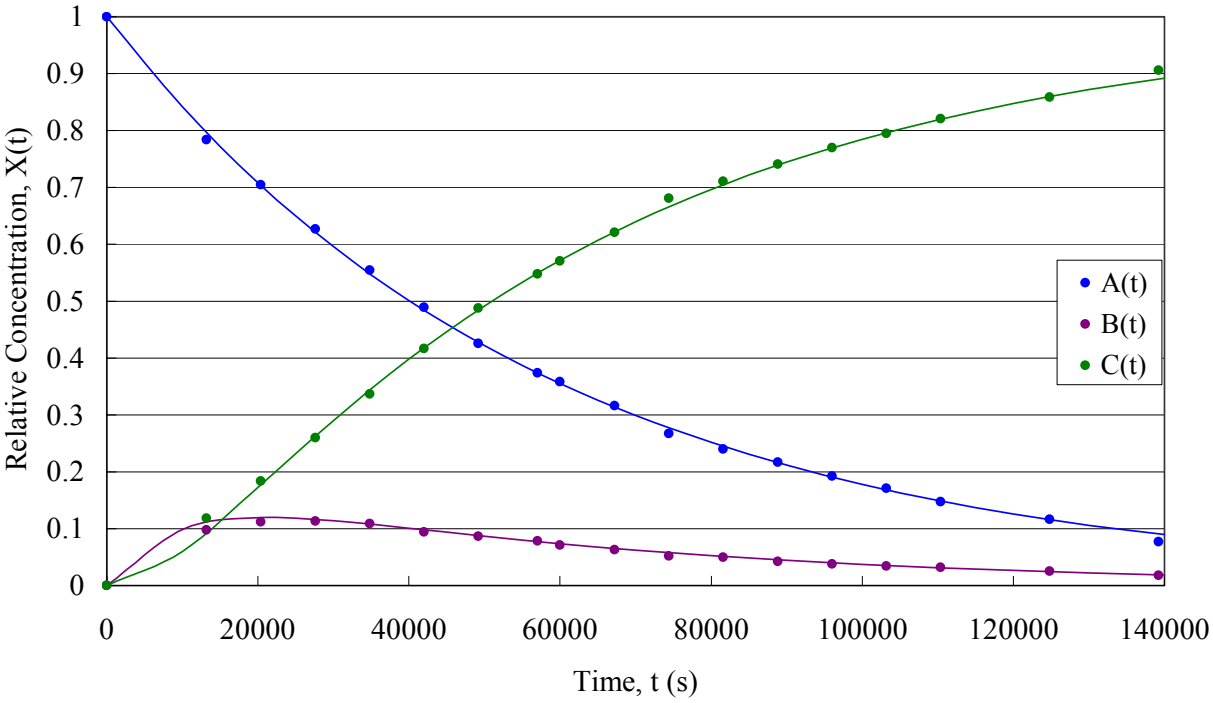
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
Time, t (s)
A(t)
B(t)
C(t)

(d)


Relative Concentration, X(t)
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0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20000
40000
60000
80000
100000
120000
140000
Time, t (s)
A(t)
B(t)
C(t)

(e)

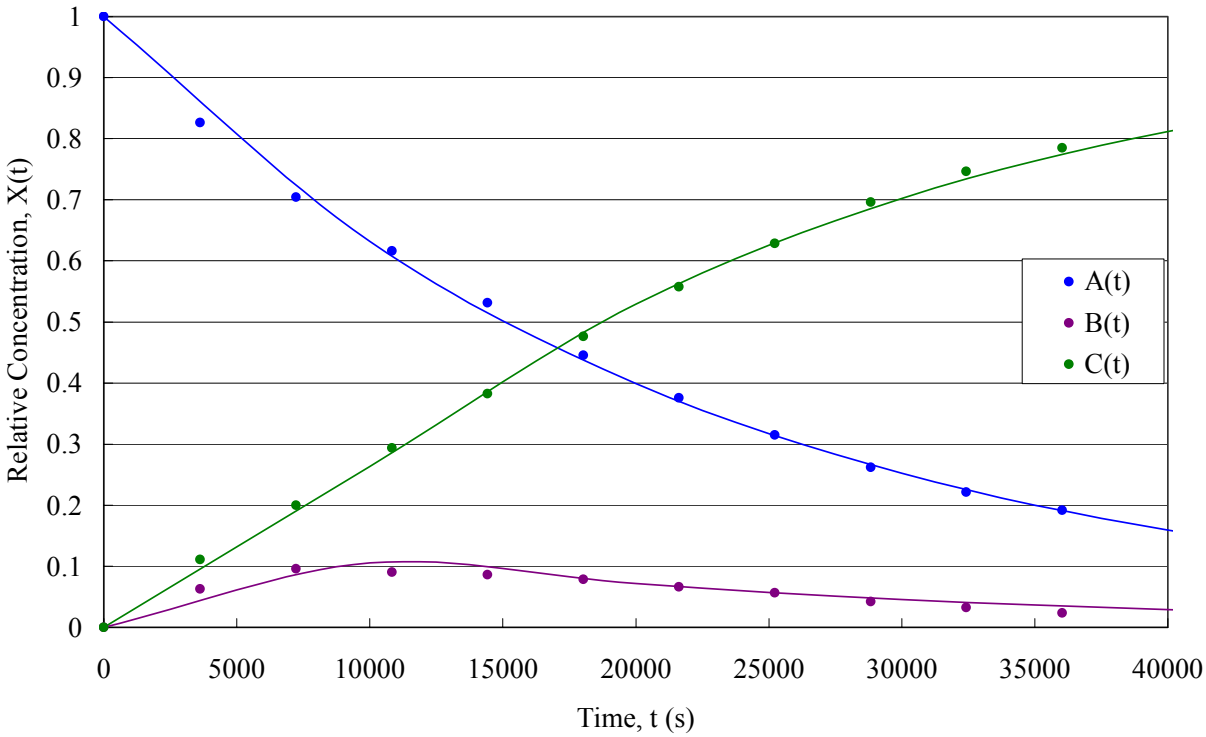

Figure 1 Time dependent concentrations of A = **4**, B = **5a** and C = **3c** at temperature, T (a) T = 405K, (b) T = 413K, (c) T = 423K, (d) T = 435K, (e) T = 443K. Points represent experimentally estimated results from time dependent ^{1}H NMR spectroscopy. Solid lines represent concentrations simulated by the two consecutive reaction first order equations, given k_1, from which rate constants k_3 were determined by simulating the experimental data points for the isomerization of **4**.

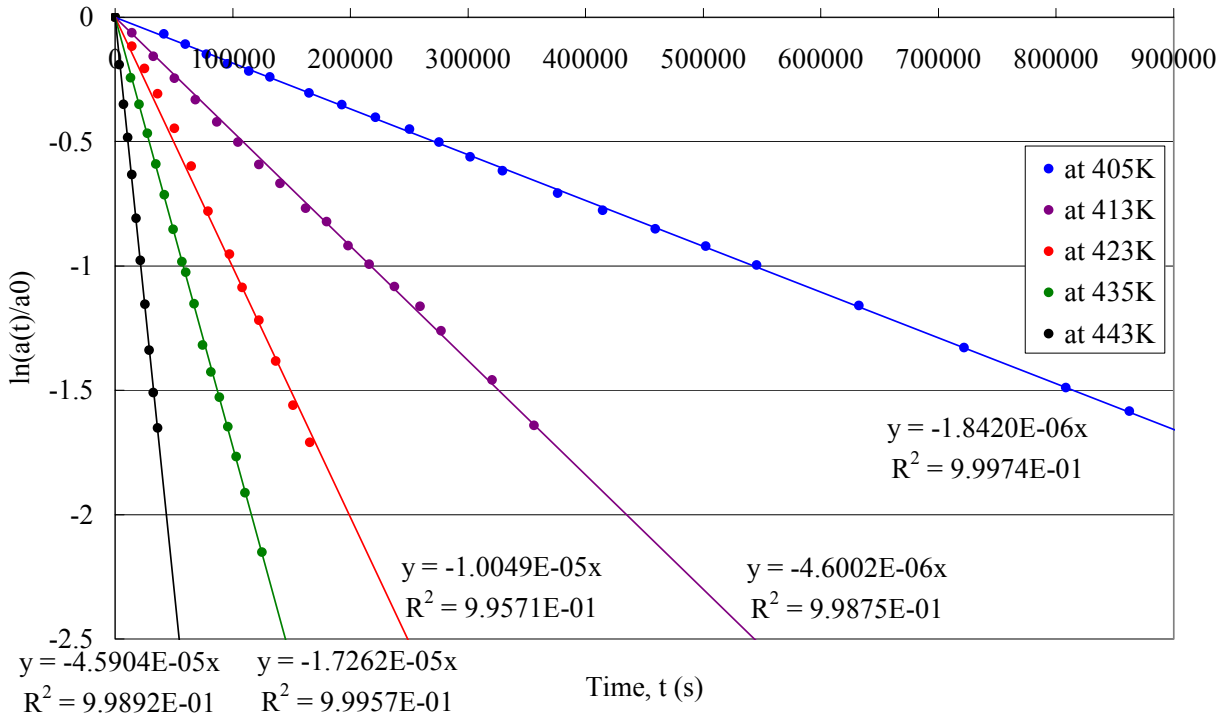

Figure 2 Thermal isomerization rate constants, $k_1(T)$, for the reaction of **4** to **5a**.

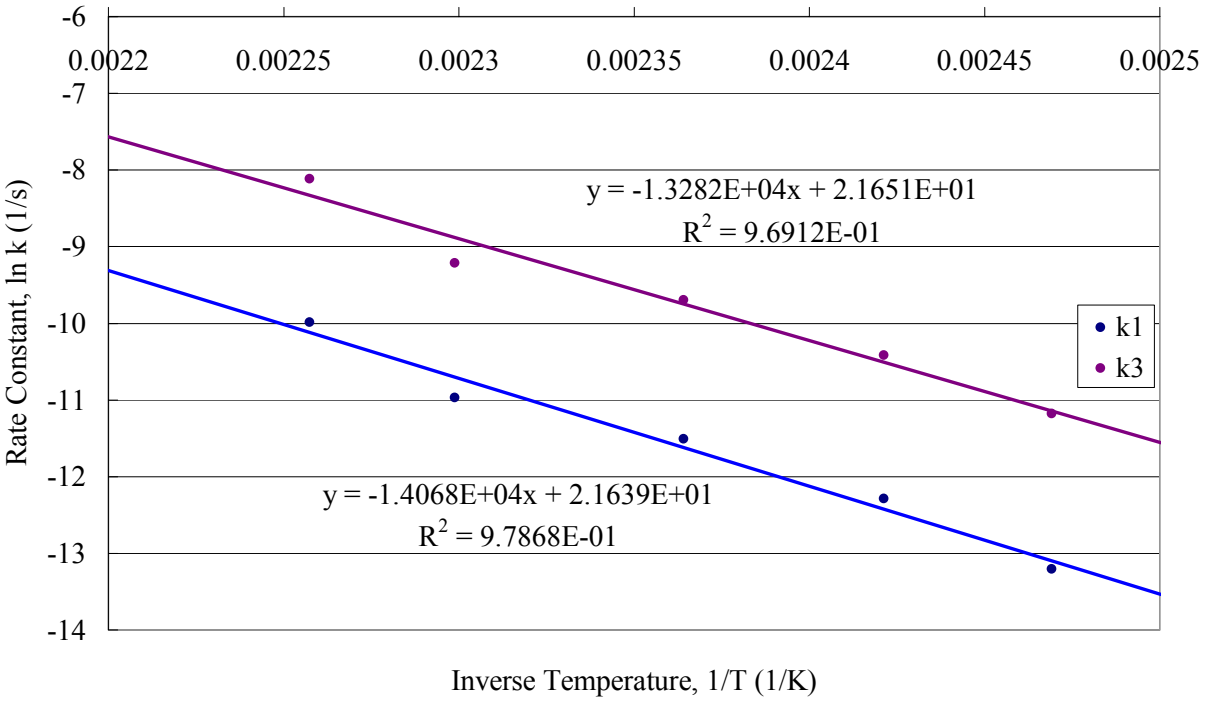

Figure 3 Arrhenius plots of k_1 and k_3 for the isomerization of **4**.

Computational Methods:

All calculations, DFT and AM1, were conducted in the gas phase. The geometry of structures optimized using DFT were all done so at the B3LYP/6-31G*(d,p) level of theory for which resulting stationary points are listed below. Concurring vibrational analysis results confirmed the stationary points were minima for compounds and saddle points for transition states respectively.

Cartesian Coordinates of Stationary Points Found for Structures Optimized at the B3LYP/6-31G*(d,p) Level of DFT:

2-Methoxyazepinium (**2c**)

6	0	1.559701	-1.410743	0.000006
6	0	2.427450	-0.282571	0.000217
6	0	2.069994	1.046009	0.000140
6	0	0.754235	1.587830	-0.000203
7	0	-0.428810	1.012487	-0.000332
6	0	-0.700768	-0.300050	-0.000244
6	0	0.190030	-1.427966	-0.000193
8	0	-1.958437	-0.659581	0.000114
6	0	-3.019404	0.342144	0.000323
1	0	2.047506	-2.381780	0.000023
1	0	3.491566	-0.504221	0.000426
1	0	2.869785	1.781215	0.000281
1	0	0.703577	2.677050	-0.000421
1	0	-0.313736	-2.390357	-0.000284
1	0	-2.940531	0.960135	-0.894260
1	0	-2.939735	0.960664	0.894466
1	0	-3.936694	-0.241385	0.000895

2-Phenyl-7-methoxy-2*H*-azepine (**1g**)

6	0	2.147756	0.451112	-0.253090
6	0	2.871528	-0.772089	-0.621298
6	0	2.592595	-1.998070	-0.113810
6	0	1.511196	-2.308321	0.804125
6	0	0.348681	-1.629523	0.850176

6	0	0.031774	-0.549831	-0.168443
7	0	0.910492	0.598267	0.044944
6	0	-1.435414	-0.144996	-0.128523
6	0	-1.852626	1.082098	0.394262
8	0	2.998369	1.511473	-0.217020
6	0	2.423588	2.777461	0.113145
6	0	-3.210341	1.405265	0.443034
6	0	-4.167078	0.506577	-0.029285
6	0	-3.757900	-0.720851	-0.555079
6	0	-2.401848	-1.041372	-0.603951
1	0	3.774669	-0.626857	-1.206766
1	0	3.288654	-2.803351	-0.342016
1	0	1.676473	-3.133429	1.493900
1	0	-0.393678	-1.858166	1.610269
1	0	0.235122	-0.981748	-1.163964
1	0	-1.100703	1.776489	0.750825
1	0	2.032246	2.775526	1.134629
1	0	1.605240	3.024687	-0.569594
1	0	3.235059	3.500558	0.019920
1	0	-3.520356	2.363689	0.850601
1	0	-5.222571	0.760686	0.007058
1	0	-4.493894	-1.425684	-0.931754
1	0	-2.088124	-1.996817	-1.019140

3-Phenyl-2-methoxy-3*H*-azepine (**3b**)

6	0	-3.052142	-0.295331	-1.000748
6	0	-3.018758	-1.568152	-0.492789
7	0	-2.360676	0.796634	-0.539132
6	0	-2.138090	-1.996615	0.561913
6	0	-1.167824	0.713704	-0.063202
6	0	-0.902604	-1.479673	0.770399
8	0	-0.626188	1.720219	0.639568
6	0	-0.292817	-0.523656	-0.223195
6	0	-1.488103	2.822664	0.955946
6	0	1.213690	-0.323192	-0.147258
6	0	1.817388	0.792237	-0.746605
6	0	3.202645	0.941352	-0.753010
6	0	4.018349	-0.026950	-0.164487
6	0	3.432492	-1.147493	0.421027

6	0	2.043676	-1.294245	0.425751
1	0	-3.811337	-0.053943	-1.742557
1	0	-3.798112	-2.250665	-0.822914
1	0	-2.504799	-2.762511	1.243498
1	0	-0.349452	-1.717387	1.674070
1	0	-0.539167	-0.902394	-1.227843
1	0	-2.357853	2.480200	1.522935
1	0	-1.836262	3.314912	0.044609
1	0	-0.881013	3.502839	1.553891
1	0	1.197940	1.556585	-1.204355
1	0	3.645586	1.817154	-1.218754
1	0	5.098127	0.089698	-0.167926
1	0	4.053851	-1.915235	0.873365
1	0	1.609319	-2.185335	0.866913

4-Phenyl-7-methoxy-4*H*-azepine (**4**)

6	0	2.664927	-0.151840	0.282469
7	0	2.606659	0.785396	-0.604374
6	0	1.699344	-0.472916	1.332447
8	0	3.782023	-0.913082	0.380586
6	0	4.849247	-0.614005	-0.524428
6	0	1.533023	1.655491	-0.716005
6	0	0.369954	-0.345706	1.178731
6	0	0.226844	1.393596	-0.518214
6	0	-0.273327	0.005643	-0.151331
6	0	-1.788004	-0.096134	-0.119974
6	0	-2.546043	0.710557	0.741514
6	0	-3.936661	0.612716	0.773912
6	0	-4.595531	-0.295023	-0.057783
6	0	-3.852723	-1.101567	-0.919746
6	0	-2.460393	-1.001096	-0.948170
1	0	2.115923	-0.814299	2.275995
1	0	5.189592	0.417726	-0.400120
1	0	4.532720	-0.748762	-1.562432
1	0	5.646328	-1.315247	-0.274315
1	0	1.820356	2.647543	-1.061491
1	0	-0.284155	-0.515784	2.031225
1	0	-0.501403	2.188129	-0.651857
1	0	0.104161	-0.703352	-0.903244

1	0	-2.042338	1.422324	1.391028
1	0	-4.506202	1.246183	1.448064
1	0	-5.678579	-0.371751	-0.033803
1	0	-4.355074	-1.810718	-1.571450
1	0	-1.888078	-1.633416	-1.622213

3-Phenyl-7-methoxy-3*H*-azepine (**5b**)

6	0	-2.544565	1.316919	-0.615166
6	0	-2.669970	0.047059	-0.083089
6	0	-1.428065	2.176052	-0.397053
7	0	-1.865556	-0.479747	0.882131
8	0	-3.816061	-0.625463	-0.374953
6	0	-4.056013	-1.858143	0.302814
6	0	-0.159790	1.763556	-0.121124
6	0	-0.593140	-0.281444	0.919412
6	0	0.209151	0.306172	-0.225376
6	0	1.689105	0.004966	-0.143301
6	0	2.471185	0.484785	0.917588
6	0	3.831532	0.186100	0.994587
6	0	4.434472	-0.598407	0.009936
6	0	3.666703	-1.081831	-1.049905
6	0	2.305593	-0.782922	-1.122603
1	0	-3.432503	1.718986	-1.093740
1	0	-1.616620	3.246615	-0.454850
1	0	-4.153242	-1.710066	1.382431
1	0	-3.253645	-2.580715	0.120892
1	0	-4.992839	-2.236351	-0.109305
1	0	0.608614	2.474868	0.166643
1	0	-0.066242	-0.529973	1.842296
1	0	-0.211361	-0.100423	-1.157849
1	0	2.013849	1.099266	1.689047
1	0	4.420630	0.567382	1.823777
1	0	5.493890	-0.829937	0.068312
1	0	4.126281	-1.691873	-1.822258
1	0	1.713402	-1.163018	-1.951020

4-Phenyl-2-methoxy-4*H*-azepine (**6a**)

7	0	-2.794922	0.553303	0.534201

6	0	-2.471068	1.771474	0.200891
6	0	-2.092402	-0.555407	0.126996
6	0	-1.386793	2.202633	-0.651669
8	0	-2.825965	-1.701123	-0.024337
6	0	-0.750299	-0.662204	-0.074048
6	0	-4.244127	-1.614361	0.090101
6	0	-0.198941	1.564314	-0.746633
6	0	0.191062	0.477393	0.236391
6	0	1.656035	0.089336	0.145058
6	0	2.186916	-0.463279	-1.029687
6	0	3.535918	-0.806593	-1.111483
6	0	4.379495	-0.603269	-0.017429
6	0	3.862771	-0.055128	1.156263
6	0	2.511653	0.288026	1.233855
1	0	-3.181511	2.537965	0.520869
1	0	-1.581933	3.073662	-1.274679
1	0	-0.349345	-1.618989	-0.391218
1	0	-4.667038	-0.894947	-0.619310
1	0	-4.553442	-1.327601	1.099355
1	0	-4.611195	-2.616495	-0.140027
1	0	0.517609	1.848641	-1.514435
1	0	-0.003462	0.851267	1.252266
1	0	1.537565	-0.629206	-1.885550
1	0	3.928330	-1.234725	-2.029522
1	0	5.430012	-0.871484	-0.080046
1	0	4.509622	0.105841	2.013925
1	0	2.115644	0.714321	2.152021

4-Phenyl-7-methoxy-2*H*-azepine (**1h**)

6	0	0.367532	1.313156	0.341045
6	0	1.691198	1.447482	0.093652
6	0	-0.358568	0.057626	0.543627
6	0	2.630859	0.327965	-0.060770
6	0	-1.787807	0.005358	0.116155
6	0	0.243849	-1.023186	1.092383
6	0	-2.274020	-1.092436	-0.611649
7	0	2.631767	-0.808396	0.528264
8	0	3.573211	0.625766	-0.994898
6	0	1.658011	-0.978480	1.607642

6	0	4.561727	-0.378156	-1.236045
6	0	-3.613718	-1.162988	-0.991072
6	0	-4.494492	-0.133663	-0.656311
6	0	-4.023318	0.966554	0.061642
6	0	-2.683662	1.037092	0.440922
1	0	-0.235152	2.216253	0.280235
1	0	2.083706	2.427550	-0.161903
1	0	-0.319035	-1.946893	1.199956
1	0	-1.587685	-1.883913	-0.896901
1	0	1.895565	-1.908174	2.131142
1	0	1.749060	-0.156898	2.337940
1	0	4.106527	-1.287083	-1.639487
1	0	5.086306	-0.639328	-0.312257
1	0	5.250781	0.056986	-1.961374
1	0	-3.966679	-2.019069	-1.558912
1	0	-5.537131	-0.186029	-0.955235
1	0	-4.701088	1.770940	0.332685
1	0	-2.338776	1.890356	1.018109

5-Phenyl-2-methoxy-3*H*-azepine (**3d**)

6	0	0.223781	1.597142	-0.270308
6	0	1.516068	1.780517	-0.669876
6	0	-0.313683	0.401870	0.360148
7	0	2.553793	0.873664	-0.647018
6	0	-1.742546	0.050724	0.100640
6	0	0.448297	-0.387851	1.161803
6	0	-2.111561	-1.263586	-0.226707
6	0	2.671436	0.006023	0.292026
6	0	1.847245	-0.003250	1.556888
8	0	3.561920	-0.997104	0.217118
6	0	-3.446233	-1.598566	-0.452440
6	0	-4.441192	-0.624725	-0.359362
6	0	-4.088235	0.686966	-0.038493
6	0	-2.753581	1.021551	0.185858
6	0	4.293346	-1.117052	-1.011594
1	0	-0.483064	2.362928	-0.577227
1	0	1.756091	2.698820	-1.202822
1	0	0.041923	-1.315459	1.554107
1	0	-1.340259	-2.021687	-0.324148

1	0	2.274278	-0.696827	2.282490
1	0	1.861751	1.012528	1.975752
1	0	-3.706959	-2.620947	-0.711175
1	0	-5.480466	-0.884026	-0.538275
1	0	-4.854422	1.452845	0.042208
1	0	-2.497427	2.042870	0.452366
1	0	4.889269	-0.219514	-1.194435
1	0	3.611382	-1.261120	-1.853804
1	0	4.937143	-1.987792	-0.884364

4-Phenyl-7-methoxy-3*H*-azepine (**5a**)

6	0	1.790600	1.408714	0.014327
6	0	2.687788	0.359777	-0.065658
6	0	0.371635	1.293914	-0.037427
7	0	2.373582	-0.921591	-0.417448
8	0	4.007240	0.685191	-0.020794
6	0	4.958964	-0.346144	-0.282515
6	0	-0.364706	0.201412	0.343152
6	0	1.285821	-1.489326	-0.023585
6	0	-1.821848	0.097577	0.117108
6	0	0.383591	-0.917488	1.032312
6	0	-2.643472	1.242498	0.109217
6	0	-4.016561	1.143841	-0.096650
6	0	-4.615022	-0.101617	-0.299338
6	0	-3.819426	-1.247062	-0.289544
6	0	-2.444672	-1.148915	-0.081479
1	0	2.228213	2.400952	-0.047843
1	0	-0.156558	2.157998	-0.433601
1	0	4.855213	-0.738927	-1.298185
1	0	4.858559	-1.175989	0.424611
1	0	5.935529	0.124920	-0.160712
1	0	0.998186	-2.415473	-0.524659
1	0	-0.284112	-1.673180	1.449047
1	0	1.003412	-0.500184	1.839029
1	0	-2.204572	2.216878	0.298159
1	0	-4.624028	2.044454	-0.087529
1	0	-5.686410	-0.177380	-0.458241
1	0	-4.267609	-2.223550	-0.449987
1	0	-1.844969	-2.053995	-0.101104

5-Phenyl-2-methoxy-4*H*-azepine (**6b**)

6	0	0.223781	1.597142	-0.270308
6	0	1.516068	1.780517	-0.669876
6	0	-0.313683	0.401870	0.360148
7	0	2.553793	0.873664	-0.647018
6	0	-1.742546	0.050724	0.100640
6	0	0.448297	-0.387851	1.161803
6	0	-2.111561	-1.263586	-0.226707
6	0	2.671436	0.006023	0.292026
6	0	1.847245	-0.003250	1.556888
8	0	3.561920	-0.997104	0.217118
6	0	-3.446233	-1.598566	-0.452440
6	0	-4.441192	-0.624725	-0.359362
6	0	-4.088235	0.686966	-0.038493
6	0	-2.753581	1.021551	0.185858
6	0	4.293346	-1.117052	-1.011594
1	0	-0.483064	2.362928	-0.577227
1	0	1.756091	2.698820	-1.202822
1	0	0.041923	-1.315459	1.554107
1	0	-1.340259	-2.021687	-0.324148
1	0	2.274278	-0.696827	2.282490
1	0	1.861751	1.012528	1.975752
1	0	-3.706959	-2.620947	-0.711175
1	0	-5.480466	-0.884026	-0.538275
1	0	-4.854422	1.452845	0.042208
1	0	-2.497427	2.042870	0.452366
1	0	4.889269	-0.219514	-1.194435
1	0	3.611382	-1.261120	-1.853804
1	0	4.937143	-1.987792	-0.884364

5-Phenyl-2-methoxy-2*H*-azepine (**7**)

6	0	0.189267	1.458215	-0.260802
6	0	-0.356009	0.271408	0.156215
6	0	1.562595	1.884490	-0.039405
6	0	0.437526	-0.769162	0.803062
6	0	-1.824434	0.044896	0.059145
6	0	-2.317647	-1.240467	-0.224267

7	0	2.636269	1.179156	-0.025289
6	0	-3.686995	-1.472245	-0.340877
6	0	1.754690	-0.970292	0.600352
6	0	-4.593176	-0.425439	-0.165508
6	0	2.510693	-0.208391	-0.455870
6	0	-4.118854	0.854212	0.128926
6	0	-2.749741	1.086514	0.242001
8	0	3.766818	-0.769439	-0.764023
6	0	4.768368	-0.630284	0.235303
1	0	-0.481353	2.219040	-0.653385
1	0	1.686925	2.951707	0.171918
1	0	-0.089755	-1.402762	1.512049
1	0	-1.617856	-2.056651	-0.377182
1	0	-4.045752	-2.470827	-0.572560
1	0	2.291404	-1.712022	1.185226
1	0	-5.660502	-0.606095	-0.251602
1	0	1.947045	-0.252226	-1.400557
1	0	-4.817181	1.671718	0.282604
1	0	-2.394099	2.078447	0.502690
1	0	4.506128	-1.154334	1.166517
1	0	4.957386	0.421479	0.469328
1	0	5.671489	-1.086790	-0.175484

5-Phenyl-2-methoxy-1*H*-azepine (**8**)

6	0	0.368374	0.178125	-0.140996
6	0	-0.444538	-0.899917	-0.310896
6	0	1.840909	-0.012664	-0.061024
6	0	-0.152213	1.556268	-0.096055
6	0	-1.894161	-0.926487	-0.424449
6	0	2.737628	0.863540	-0.700194
6	0	-1.346775	1.933905	0.375416
6	0	4.114385	0.654943	-0.642900
6	0	-2.730065	-0.038395	0.163077
7	0	-2.305145	1.048494	0.943432
8	0	-4.088946	-0.074385	0.131487
6	0	-4.719794	-1.173894	-0.516112
6	0	4.636040	-0.431722	0.060838
6	0	3.762417	-1.306246	0.708772
6	0	2.385921	-1.095555	0.653633

1	0	0.039976	-1.866492	-0.438378
1	0	0.489506	2.349830	-0.465962
1	0	-2.323629	-1.743824	-0.990861
1	0	2.357124	1.702309	-1.275026
1	0	-1.639958	2.981632	0.351882
1	0	4.781910	1.342123	-1.155565
1	0	-3.097967	1.519792	1.358719
1	0	-4.407436	-2.124780	-0.069759
1	0	-4.490045	-1.184061	-1.587700
1	0	-5.791544	-1.033019	-0.372391
1	0	5.709309	-0.590443	0.109272
1	0	4.153771	-2.148102	1.273377
1	0	1.717793	-1.760755	1.191816

TS1

6	0	-2.203885	-0.365379	0.009934
7	0	-2.630179	0.912413	-0.240432
6	0	-1.731549	-1.168508	-1.166265
8	0	-2.948386	-1.106460	0.894577
6	0	-3.693818	-0.380810	1.872081
6	0	-1.771554	1.766064	-0.790082
6	0	-0.487583	-0.832627	-1.508817
6	0	-0.396573	1.532197	-0.907639
6	0	0.126641	0.230261	-0.631172
6	0	1.534686	0.072552	-0.170914
6	0	2.246001	-1.115060	-0.409272
6	0	3.560275	-1.262413	0.030563
6	0	4.188489	-0.228876	0.726663
6	0	3.486893	0.949956	0.989373
6	0	2.173098	1.095536	0.551763
1	0	-2.406173	-1.825540	-1.703648
1	0	-4.503806	0.192751	1.413598
1	0	-3.051631	0.310911	2.430092
1	0	-4.100603	-1.132871	2.550376
1	0	-2.160486	2.762474	-0.995089
1	0	0.024461	-1.164150	-2.407076
1	0	0.263145	2.388567	-1.018033
1	0	-0.910464	-0.120148	0.383506
1	0	1.763734	-1.930054	-0.939449

1	0	4.093601	-2.187256	-0.169286
1	0	5.211841	-0.344364	1.071296
1	0	3.961405	1.753557	1.545109
1	0	1.626596	2.003543	0.787720

TS2

6	0	-0.498818	1.005644	0.342552
6	0	0.308824	-0.042570	-0.197400
6	0	-1.531097	1.578658	-0.575015
6	0	-0.346982	-1.159213	-0.764666
6	0	1.779225	-0.034046	-0.028007
6	0	2.503574	-1.226178	0.164750
7	0	-2.588505	0.903380	-0.806529
6	0	3.886643	-1.207606	0.325431
6	0	-1.705282	-1.359800	-0.611473
6	0	4.583164	0.002656	0.302029
6	0	-2.543564	-0.334259	-0.057053
6	0	3.881703	1.194206	0.114970
6	0	2.498105	1.175363	-0.050968
8	0	-3.756122	-0.796403	0.392469
6	0	-4.624054	0.187448	0.947672
1	0	0.019724	1.720689	0.984598
1	0	-1.361075	2.529670	-1.080475
1	0	0.250273	-1.948798	-1.209753
1	0	1.972525	-2.170894	0.221755
1	0	4.421227	-2.140153	0.481714
1	0	-2.146658	-2.332706	-0.811256
1	0	5.661611	0.016029	0.428432
1	0	-1.606975	0.166985	0.863780
1	0	4.413493	2.140882	0.086181
1	0	1.968052	2.105775	-0.229538
1	0	-4.861742	0.968193	0.219234
1	0	-4.176302	0.650478	1.837609
1	0	-5.534289	-0.340398	1.236734

TS3

6	0	-1.812677	-1.179188	0.710006
6	0	-2.628436	-0.270921	-0.027293

6	0	-0.408210	-1.334967	0.240540
7	0	-2.337719	1.016966	-0.256387
8	0	-3.845713	-0.716593	-0.390424
6	0	-4.778177	0.232150	-0.928930
6	0	0.386918	-0.278727	0.494594
6	0	-1.326850	1.553895	0.423933
6	0	1.807898	-0.130606	0.132314
6	0	-0.372810	0.823332	1.190351
6	0	2.633540	-1.262155	-0.011910
6	0	3.975420	-1.131358	-0.356413
6	0	4.533138	0.134441	-0.555048
6	0	3.731847	1.266042	-0.405439
6	0	2.385526	1.135413	-0.065648
1	0	-2.336601	-2.079131	1.035479
1	0	-0.108013	-2.218299	-0.314731
1	0	-4.407480	0.657531	-1.864340
1	0	-4.962401	1.046180	-0.223208
1	0	-5.692111	-0.336280	-1.104965
1	0	-1.340433	2.644997	0.471652
1	0	0.209068	1.431480	1.885439
1	0	-1.309440	-0.122904	1.622663
1	0	2.218990	-2.248742	0.171384
1	0	4.592358	-2.019713	-0.458607
1	0	5.581714	0.235622	-0.818762
1	0	4.152793	2.255715	-0.558690
1	0	1.768537	2.023424	0.028444

TS4

6	0	0.248730	1.561147	-0.324056
6	0	1.637909	1.848181	-0.186661
6	0	-0.317884	0.411824	0.239392
7	0	2.602500	0.873972	-0.639683
6	0	-1.752930	0.065902	0.040666
6	0	0.438102	-0.282164	1.205036
6	0	-2.139487	-1.280866	-0.048091
6	0	2.693938	-0.054705	0.232050
6	0	1.805412	0.007259	1.442212
8	0	3.494245	-1.126438	0.137697
6	0	-3.476542	-1.633967	-0.229677

6	0	-4.455735	-0.645515	-0.328626
6	0	-4.085992	0.698225	-0.241710
6	0	-2.750239	1.050030	-0.058516
6	0	4.299214	-1.193341	-1.047948
1	0	-0.409809	2.316674	-0.745760
1	0	1.944011	2.870451	-0.412960
1	0	-0.100012	-0.918403	1.903658
1	0	-1.378541	-2.054034	0.005309
1	0	2.234133	-0.396476	2.359620
1	0	1.737967	1.445140	1.163368
1	0	-3.750751	-2.682540	-0.301975
1	0	-5.497088	-0.918065	-0.472218
1	0	-4.841613	1.475865	-0.307532
1	0	-2.483610	2.098557	0.033624
1	0	4.937690	-0.309160	-1.129224
1	0	3.666694	-1.250556	-1.938037
1	0	4.902495	-2.095812	-0.946106

TS5

6	0	-0.490263	-0.085097	1.462869
6	0	-1.490983	-0.942739	0.939937
6	0	0.373540	0.642351	0.445498
6	0	-2.437942	-0.394269	0.050931
6	0	1.734690	0.190289	0.109439
6	0	-0.311703	1.662938	-0.097809
6	0	2.677854	1.092390	-0.418009
7	0	-2.660940	0.909144	-0.014285
8	0	-3.306087	-1.258409	-0.528939
6	0	-1.704847	1.774398	0.440697
6	0	-4.443681	-0.688767	-1.180680
6	0	3.966856	0.675481	-0.736233
6	0	4.350002	-0.651782	-0.526808
6	0	3.429603	-1.555556	0.003993
6	0	2.136872	-1.139946	0.320901
1	0	0.017350	-0.428682	2.366455
1	0	-1.723252	-1.903365	1.390293
1	0	0.026910	2.293973	-0.913729
1	0	2.398646	2.132364	-0.556811
1	0	-2.091575	2.780872	0.621066

1	0	-1.262595	1.059848	1.612856
1	0	-4.140965	0.010935	-1.965534
1	0	-5.082821	-0.155674	-0.470395
1	0	-4.982149	-1.532505	-1.614413
1	0	4.678386	1.390385	-1.139523
1	0	5.357314	-0.975543	-0.771255
1	0	3.715810	-2.590302	0.169192
1	0	1.424219	-1.857178	0.714945

TS6

7	0	2.319908	0.125826	-0.989001
6	0	1.567284	1.257018	-0.891713
6	0	2.647388	-0.428906	0.298506
6	0	0.319241	1.281924	-0.270463
8	0	3.848294	-0.138375	0.843067
6	0	1.700356	-1.194787	0.854267
6	0	4.919509	0.179743	-0.051439
6	0	-0.328772	0.057594	-0.006444
6	0	0.452984	-1.146822	0.035778
6	0	-1.812612	0.019971	0.014057
6	0	-2.533055	-1.017137	-0.604219
6	0	-3.925372	-1.037031	-0.570059
6	0	-4.630063	-0.030066	0.092689
6	0	-3.927775	1.001619	0.716485
6	0	-2.535041	1.030459	0.672548
1	0	1.839872	2.104090	-1.526010
1	0	-0.263808	2.195761	-0.326304
1	0	1.796443	-1.765082	1.769453
1	0	4.732352	1.115212	-0.585774
1	0	5.080245	-0.618355	-0.783316
1	0	5.802339	0.284516	0.581345
1	0	-0.124421	-2.071165	0.007697
1	0	1.268349	-0.784550	-1.037555
1	0	-2.001682	-1.797977	-1.139040
1	0	-4.461786	-1.840350	-1.066696
1	0	-5.715264	-0.050522	0.122970
1	0	-4.463971	1.785949	1.242816
1	0	-1.998810	1.827214	1.178936

TS7

6	0	2.557782	-0.303351	0.166156
7	0	2.015157	0.704977	-0.553490
6	0	1.815302	-1.014911	1.133820
8	0	3.740351	-0.840848	-0.187778
6	0	4.476726	-0.193647	-1.234206
6	0	1.503437	1.771250	0.270510
6	0	0.439272	-0.861479	1.130828
6	0	0.274271	1.573908	0.745897
6	0	-0.239333	0.197840	0.421192
6	0	-1.685015	0.018343	0.097562
6	0	-2.540611	1.121296	-0.069287
6	0	-3.887816	0.949267	-0.382715
6	0	-4.417008	-0.331340	-0.547047
6	0	-3.577054	-1.437640	-0.409058
6	0	-2.229581	-1.263916	-0.100886
1	0	2.283051	-1.846180	1.649992
1	0	4.574318	0.877405	-1.040621
1	0	3.985081	-0.329702	-2.200512
1	0	5.454808	-0.676196	-1.237950
1	0	2.128584	2.647620	0.401298
1	0	-0.154646	-1.642169	1.603035
1	0	-0.291825	2.287110	1.334794
1	0	0.743041	0.215233	-0.625840
1	0	-2.146833	2.126509	0.039765
1	0	-4.525437	1.820970	-0.500897
1	0	-5.466124	-0.465339	-0.793321
1	0	-3.968850	-2.440519	-0.554471
1	0	-1.586305	-2.136524	-0.035216