Research Article

Journal of Physical Organic Chemistry

Received: 11 May 2007, Revised: 14 September 2007, Accepted: 17 September 2007, Published online in Wiley InterScience: 5 December 2007

(www.interscience.wiley.com) DOI 10.1002/poc.1280

6,7-diaza-1-methoxy- 5-methyl-2, 8-dioxabicyclo[3.2.1]oct-6-ene. An unstable bicyclic precursor of a dioxa carbonyl ylide and carbenes by ylide ring opening

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Synthesis of a bicyclic 2,2-dioxa oxadiazoline (6,7-diaza-1-methoxy-5-methyl-2,8-dioxabicyclo[3.2.1]oct-6-ene) is reported. Its thermolysis at 27°C is about 200 times as fast as the thermolysis of a monocyclic oxadiazoline model system. Presumably, a cyclic dioxa carbonyl ylide is formed initially and the ylide then undergoes a bond scission to afford either a dioxacarbene or a dialkylcarbene or it cyclizes to an oxirane. A small fraction of a dialkylcarbene was trapped as the product of addition to dimethyl acetylenedicarboxylate (DMAD). Computations of the barriers to the loss of N_2 from the oxadiazolines and to the formation of the carbenes from the carbonyl ylide resulting from thermolysis of the bicyclic oxadiazoline are compared to corresponding barriers for a similar monocyclic oxadiazoline. The rate acceleration is accounted for in terms of geometric factors. The complex products from the decomposition of the bicyclic oxadiazoline were not studied. Copyright © 2007 John Wiley & Sons, Ltd.

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Keywords: bicyclic oxadiazoline; carbene; carbonyl ylide; DMAD; kinetics; DFT calculations

INTRODUCTION

Having studied a variety of 2,2-dialkoxy oxadiazolines, we decided to attempt the preparation of a bicyclic analogue in order to determine the effect of structure on the stability of the starting materials and the intermediates. We were particularly interested in the stability of the carbonyl ylide (**5**) that would be formed by 1,3-dipolar cycloreversion with extrusion of N_2, Schemes 1, 2. A cyclic ylide, such as **5**, could be more stable than an acyclic analogue, such as **2**,[1a] because **5** is constrained to be nearly planar by the other atoms in the ring and might be trappable as an adduct of a dipolarophile (**6**), Scheme 2.

RESULTS AND DISCUSSION

The bicyclic oxadiazoline (**4**) shown in Scheme 3 was prepared by oxidative cyclization of a mixture of hydrazones **7** with lead tetraacetate according to prescribed procedures,[1b] modified to take into account the unexpected properties of **4**. Part of the starting material **7** probably afforded intermediate **8**, which was not isolated but assumed to be largely converted to **4** by treatment of the crude cyclization product with catalytic trifluoroacetic acid.[2]

Co-products of the oxidation of **7** were diastereomers **8**, compound **9** (*ca.* 9%), and acyclic compound **11**. It is unclear whether the oxidation occurs by coordination of the lead oxidant to the oxygen of the hydroxyl group or to the NH function (or either) of **7**. We have postulated intermediates analogous to **10** previously[3] and adherence to that mechanism would have **4**, **8** and **11** formed according to Scheme 4. Possible mechanisms of formation of **9** are discussed below.

Although it is difficult to account for **9** from **10**, there is a rationale based on transfer of the CO_2Me group from N onto O of the alcohol function, Scheme 5. Formation of a *cis*, 7-membered ring (**12**) is reasonable because the $Pb(OAc)_3$ group of **10** is larger than the CO_2Me group, making the structure **12** likely. A similar, but less likely, process could begin with the lead function attached to the hydroxyl oxygen (**14**), Scheme 5. It is less likely because the favored configuration of **14** is expected to be one that would keep the CO_2Me group remote from the $OPb(OAc)_3$ group but formation of a 7-membered intermediate, such as **15**, from **10** could possibly be involved. The postulated species **13** is

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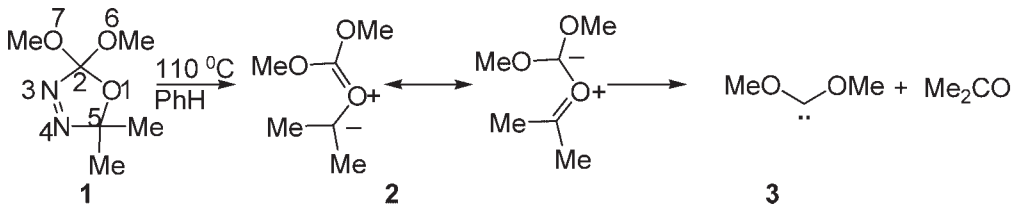
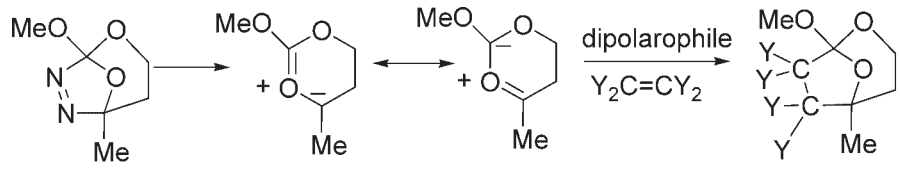


1 2 3

Scheme 1.



4 5 6

Scheme 2.

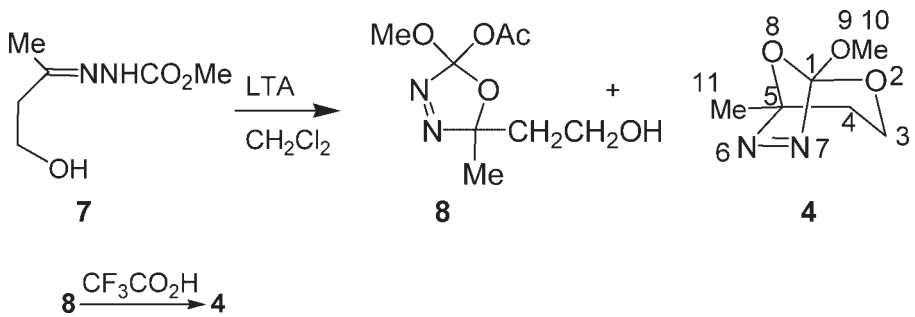
at the right oxidation state to lead to **9**, but the steps that would take it there are purely speculative, Scheme 5.

Compound **4** was surprisingly unstable. Solutions of **4** in benzene or in methylene chloride evolved bubbles at room temperature; a property that we had not observed with a large number of monocyclic oxadiazolines such as **1**.[4] The rate constant for thermolysis of **4** (Scheme 6) in benzene-D6 was determined by periodic integration of a ^{1}H signal (from CH_2CH_2O) at 2.97δ in the NMR spectrum of **4**, and the benzene signal, in the probe of a 200 MHz NMR spectrometer operating at 27°C. Standard first order treatment of the ratios obtained by division of that integral by the benzene integral gave $k_{27°C} = 1.6 \times 10^{-5}\,s^{-1}$, with $r^2 = 0.996$. At 110°C, in benzene in a sealed tube, the rate constant for thermolysis of the monocyclic oxadiazoline **1** is about $2.4 \times 10^{-5}\,s^{-1}$.[1] That makes thermolysis of **4** a factor of *ca.* $0.67 \times 2^{8.3}$ (or about 200) faster than that of **1**, assuming that each 10° rise in temperature would increase the rate by a factor of two. We were intrigued by this unexpected rate factor and decided to look for possible reasons by means of computation. We also looked for precedents from the literature of the kinetics of thermolysis of bicyclic azo compounds.

COMPUTATIONAL STUDIES

Calculations were carried out with GAUSSIAN 03[5] at the B3PW91/6-31 + G** level of theory. Vibration analyses were performed for all structures in order to confirm minima and transition states and evaluate reaction barriers. The calculated free energy of activation for thermolysis of **1** to the carbonyl ylide **2** at 383 K (110°C), the usual experimental temperature, was found to be 32.9 kcal mol^{-1}, Table 1, in good agreement with the experimental value of 32.6 kcal mol^{-1}, determined from the rate constant, the temperature and the equation $\log k = \log A - E_a/2.303RT$, with $\log A = 14$. Most of **1** affords dimethoxycarbene (**3**) and acetone.[4] The corresponding calculated free energy of activation for thermolysis of **4** at 27°C (300 K) is 23.7 kcal mol^{-1}, again in acceptable agreement with the experimental value of 25.8 kcal mol^{-1}, determined with $\log A = 14$. Calculated barriers for thermolysis of **1** and **4** to their respective ylides are likely to be valid because the reactions are very similar. The calculated free energies of activation for extrusion of N_2 from **1** and **4** to form their respective carbonyl ylides at 110 and 27°C are different by 9.2 kcal mol^{-1} (32.9–23.7). Experimentally, they are different by 6.8 kcal mol^{-1} (32.6–25.8). Either difference indicates that, if **4** extrudes N_2 slowly at 27°C, **1** should appear to be stable at that temperature, in accord with experiment, Fig. 1.

Inspection of the computed geometric changes that accompany the fragmentations of **4** and **1** suggested a possible reason for the difference. In **4**, the improper dihedral angle, C5N6C1O8 (as in numbering systems in Schemes 1 and 3), is 24.5°. In the transition state leading to the carbonyl ylide, it is 27.0°, a change of less than 3°. In **1**, the corresponding angle, C5N3C2O1 is 8.7° and at the transition state for its thermolysis to **2** that angle changes to 23.5°, a change of about 18°. In short, the nearly planar **1** is considerably distorted when the transition state for



7 8 4

Scheme 3.

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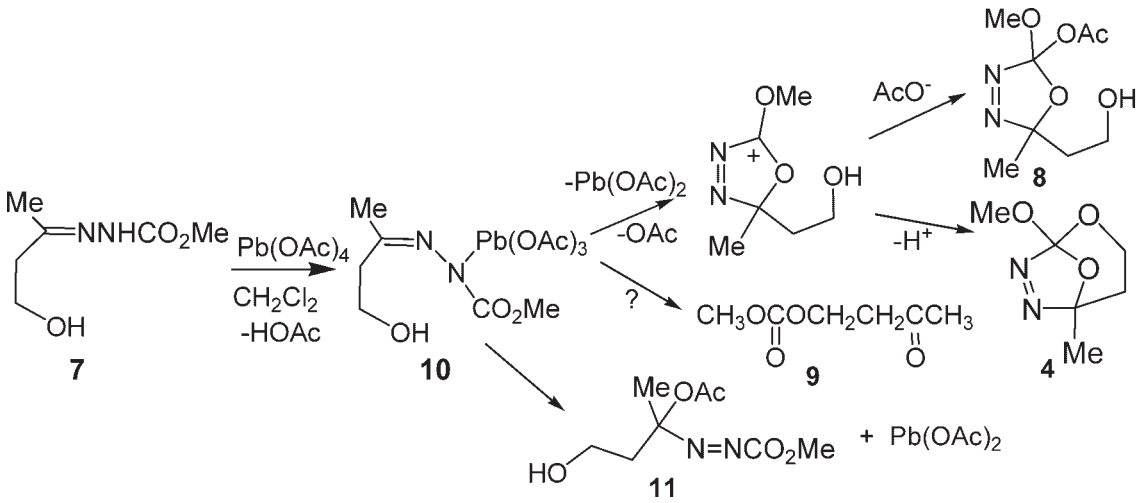


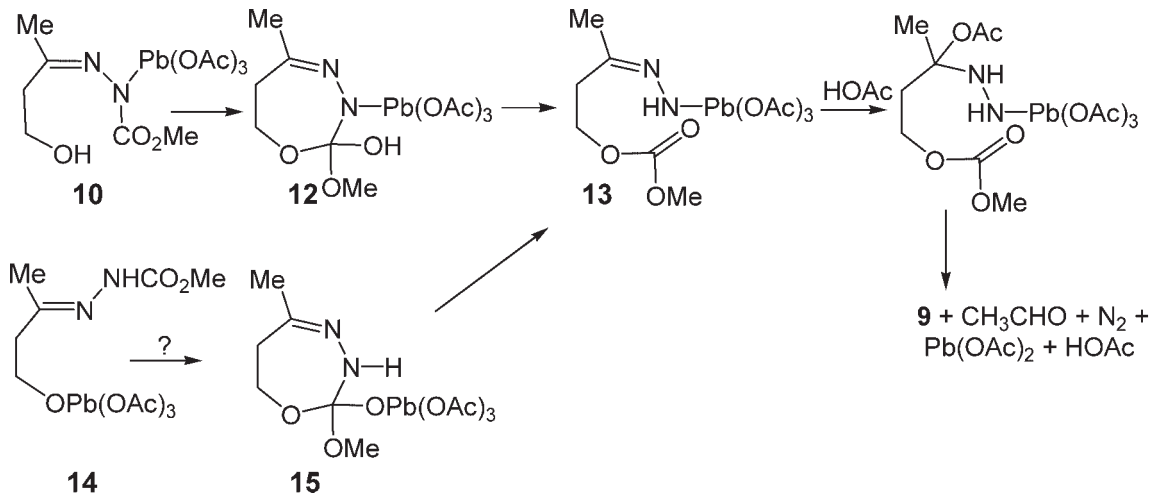
Scheme 4.

extrusion of N_2 is reached whereas in **4**, which is farther from planarity to begin with, the corresponding angle change is less than 3°. In the language of the Principal of Least Motion,[6] there is a much smaller change of geometry for extrusion of N_2 from **4**, compared to the geometric change for extrusion of N_2 from **1**. There are other differences, such as strain in **4** (not likely to be large)[7] between the geometric changes involved for analogous reactions of **4** and **1**, but we have focused on the one that is probably the largest.

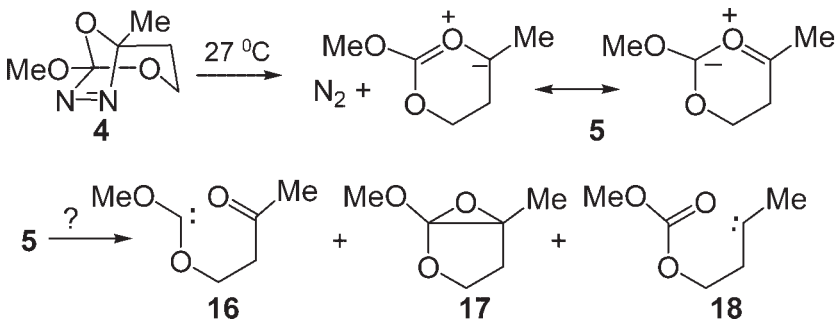
The computations indicate that if carbonyl ylides are real intermediates in thermolysis of both oxadiazolines, they must be very short lived. In the case of the ylide from **4**, the ylide lies in a shallow free energy well that is about 12.7 kcal mol^{-1} below the transition state leading to it and only about 0.7 kcal mol^{-1} below the transition state for its fragmentation to carbene **16** (Fig. 1) and 0.8 kcal mol^{-1} below the transition state leading to **18**, at 300 K. In the case of **1**, the free energy difference between the ylide and the transition state leading to it is 14.5 kcal mol^{-1}. The free energy barrier for fragmentation of the ylide to the carbene is only 0.8 kcal mol^{-1}, at 383 K. Although the numbers and the errors in computational estimates of barriers make it conceivable that the extrusion of N_2 and the fragmentation of the carbonyl ylide are concerted, a carbonyl ylide is an intermediate in each case according to IRC calculations. A carbonyl ylide is also likely on the basis of theory, the reverse reaction (addition of such an ylide to an alkene) being well known.[8] Smith had concluded earlier, on the basis of calculations at a lower level of theory, that thermolysis of a compound analogous to **1** can be fully concerted, affording N_2, a dialkoxycarbene, and acetone in a single step.[9] With higher level calculations on analogous systems, we have found that a carbonyl ylide is an actual intermediate.[10a–e]

Ylide **5** is of higher free energy than the isomeric carbenes **16** or **18** (Fig. 1). We are not sure of the reasons, but entropy and the fact that the product of ylide fragmentation has the stable carbonyl group are probably contributing factors. For example, ylide **5** and carbene **16** have entropies of 96.9 and 107.3 cal K^{-1}, respectively.

Precedents from the literature were sought, from the kinetics of thermolysis of bicyclic azo compounds. The latter are not really good models; however, because many bicyclic azo compounds



Scheme 5.



Scheme 6.

extrude N_2 by a stepwise mechanism[11] and afford singlet diradical intermediates, whereas **4** affords a carbonyl ylide.[10b] Azo compounds are therefore not useful compounds for comparison to **4**.

The products from thermolysis of **4** were very numerous. Capture of either the ylide **5** or the carbenes **16** or **18** by addition to neat dimethyl acetylenedicarboxylate (DMAD) to afford **19** was successful but the yield was low, as expected (Scheme 7). Either the ylide **5** or carbene **18,** derived from it, could react with DMAD to afford the product (**19**) that was isolated, Scheme 7. The ylide route is unlikely because of the ylide's short calculated lifetime. There were many major signals, and numerous minor signals, in addition to those from excess DMAD, in the ^{1}H NMR spectrum of the crude. Addition of the ylide to DMAD was clearly not a major process, in keeping with the calculation of a very small barrier to fragmentation of the ylide to carbene **16**, Scheme 6, or fragmentation to carbene **18**. The reaction of carbene **18** with DMAD to produce **19** is pictured as concerted, Scheme 7.

Cyclization of carbene **16** (or ylide **5**) to oxirane **17**, Scheme 6, is another intramolecular process that should also occur with a small barrier. We have previously shown that dimethoxycarbene reacts with an intramolecular carbonyl group to form complex products.[12] In the case of **4**, the numerous products of thermolysis were not identified. The intermediacy of **18**, suggested by the formation of **19** and by numerous NMR signals between 5 and 6δ in the spectrum of the crude, might alone lead to three olefinic products from 1,2-migration of hydrogen.

CONCLUSIONS

A bicyclic oxadiazoline undergoes 1,3-cycloreversion (loss of N_2) about 200 times as fast as a monocyclic analogue. The cyclic carbonyl ylide produced is not more stable than an acyclic analogue, but fragments to carbenes over a very small energy barrier. Ylide **5** probably rearranges to carbenes **16** and **18**. The latter carbene was captured with DMAD to afford cyclopropene **19**.

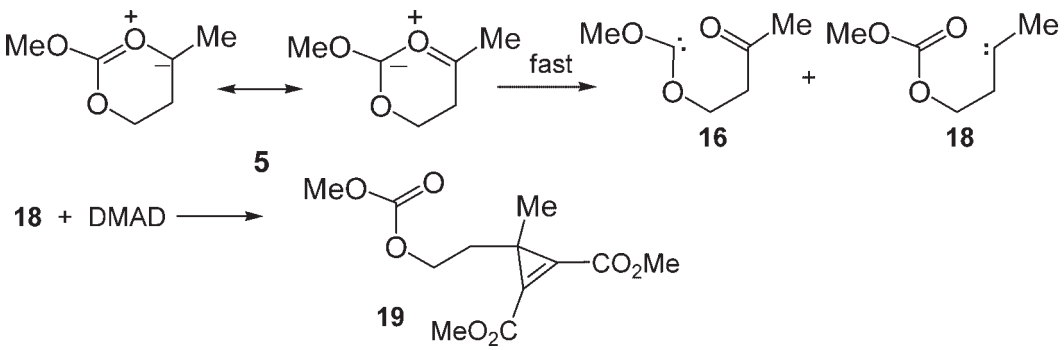
EXPERIMENTAL

General instrumentation

^{1}H NMR spectra were taken with a Bruker AV 200 instrument and are referenced to residual H in $CDCl_3$ at 7.26 ppm or to residual H in C_6D_6 at 7.16 ppm. ^{13}C NMR spectra, acquired with the same instrument, are referenced to the centerline of the $CDCl_3$ triplet at 77.2 ppm or to the centerline of the C_6D_6 triplet at 128.1 ppm. High-resolution mass spectra, with a Micromass GCT, TOF instrument, were acquired in the CI (NH_3) or EI modes. Infrared spectra were measured on neat samples between NaCl plates, with a Biorad FTIR spectrometer.

Synthesis of kinetic **7**

A 2.6:1 mixture of (E/Z) isomers (the hydrazone of 2-butanone is 78%(E), 22%(Z)[13]) was prepared from the methyl ester of



Scheme 7.

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Table 1. Temperatures and calculated activation parameters for thermolysis of oxadiazolines to carbonyl ylides and for fragmentation of the ylides

Compound	Temperature (K)	Calculated parameters for ylide formation (ylide fragmentation)		
		$\Delta G^{\#}$ (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal K^{-1})
1	383	32.9 (0.8)	37.5 (0.16)	13 (−1.58)
4	300	23.7 (0.7)	29.8 (−0.20)	20 (−2.83)

hydrazinecarboxylic acid and 4-hydroxy-2-butanone in 81% yield. Major isomer (2.6 parts): ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 2.47 (m, 3H)(CH_2 + OH), 3.74 (s), 3.82 (m) (overlapping with each other and with signals from the minor isomer); minor isomer (1 part) ^{1}H NMR δ: 2.00 (s), 3.74 (s, shoulder on 3.76), 3.82 (m); the total area of the overlapping signals at 3.74–3.85δ agreed well with the expected value calculated from the singlets at 1.83 and 2.00δ; ^{13}C NMR of the composite (50.3 MHz, $CDCl_3$) δ: 15.7, 23.8, 34.3, 40.6, 52.9, 59.1, 59.3, 152.7, 154.8 (br), 155.5. HRMS (EI) *m/z*: calcd for $C_6H_{12}N_2O_3$, 160.0848 found 160.0852. The minor isomer isomerized to the major isomer during long storage (*ca.* 1 year) at room temperature. Presumably, the mixture obtained initially reflects kinetic control (at least in part) and the old material is the thermodynamic product.

Thermodynamic hydrazone **7**

Colorless solid, obtained by long storage of kinetic **7**, mp 70–71°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 2.52 (t, J = 5.5 Hz, 2H), 3.07 (br. t, 1H, OH), 3.81 (s, 3H), 3.83–3.94 (m, 2H), 7.68 (br. s, NH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 15.9, 40.7, 53.0, 59.4, 152.5, 154.8.

Synthesis of bicyclic oxadiazoline **4**

Oxidative cyclization of the thermodynamic hydrazone **7** (2.04 g, 12.74 mmol) with lead tetraacetate (6.15 g of 95%, 13.18 mmol) in methylene chloride (44 ml) was carried out at 0°C during 1 h. Subsequent addition of trifluoroacetic acid (*ca.* three drops) at 0°C, stirring for 1 h, extraction with aqueous $NaHCO_3$ (2 × 25 ml), drying over $MgSO_4$, and very fast chromatography through a column of silica (2 × 8 cm), eluting with 1:1 ether/pentane, gave **4** (0.28 g, 1.76 mmol, 13.8%) as a colorless oil. ^{1}H NMR (200 MHz, C_6D_6) δ: 0.91 (dd, J = 5.1 and 13.8 Hz, 1H), 1.25–1.40 (m, 1H), 1.43 (s, 3H), 2.97 (dt, J = 5.2 and 11.7 Hz, 1H), 3.34–3.43 (m, 1H). 3.52 (s, 3H); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.62 (dd J = 5.1 and 13.8 Hz, 1H), 1.81 (s, 3H), 1.86–2.02 (m, 1H), 3.27 (dt, J = 5.1 and 11.8 Hz, 1H), 3.70 (s, 3H), 3.92 (dd, J = 7.2 and 11.7 Hz, 1H); ^{13}C NMR (50.3 MHz, C_6D_6) δ: 20.0, 27.8, 52.7, 61.3, 113.0, 131.4; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 20.0, 27.8, 52.9, 61.3, 113.0, 130.5; HRMS (CI, NH_3) *m/z*: calcd for $C_6H_{14}N_3O_3$ $(M + NH_4)^+$, 176.1035 found 176.1030. After **4** came a mixture believed to be the uncyclized diasteriomers **8** (not isolated), then byproduct **9** and finally, with ether alone as eluent, compound **11**, Scheme 4.

Kinetics of thermolysis of **4**

Thermolysis of **4** (Scheme 6) (10 mg in 0.8 ml of C_6D_6) was followed by means of NMR spectroscopy. The rate constant was determined by periodic integration of a ^{1}H signal (from CH_2CH_2O) at 2.97δ in the NMR spectrum of **4**, and the benzene signal, in the probe of a 200 MHz NMR spectrometer operating at 27°C. Standard first order treatment of the ratios obtained by division of the integral at 2.97δ by the benzene integral gave $k_{27°C} = 1.6 \times 10^{-5}$ s^{-1}, with $r^2 = 0.996$. At 110°C, in benzene in a sealed tube, the rate constant for the thermolysis of the monocyclic oxadiazoline **1** is about 2.4×10^{-5} s^{-1}.[1]

*Methyl 3-oxobutylcarbonate (***9***)*

Very pale yellow oil. Yield 8.8%, IR (neat, cm^{-1}) 1752 and 1721; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.13(s, 3H), 2.76 (t, J = 6.3 Hz, 2H), 3.71 (s, 3H), 4.33 (t, J = 6.3 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 30.25, 42.06, 54.79, 62.65, 155.54, 205.24; HRMS (CI, NH_3) *m/z*: calcd

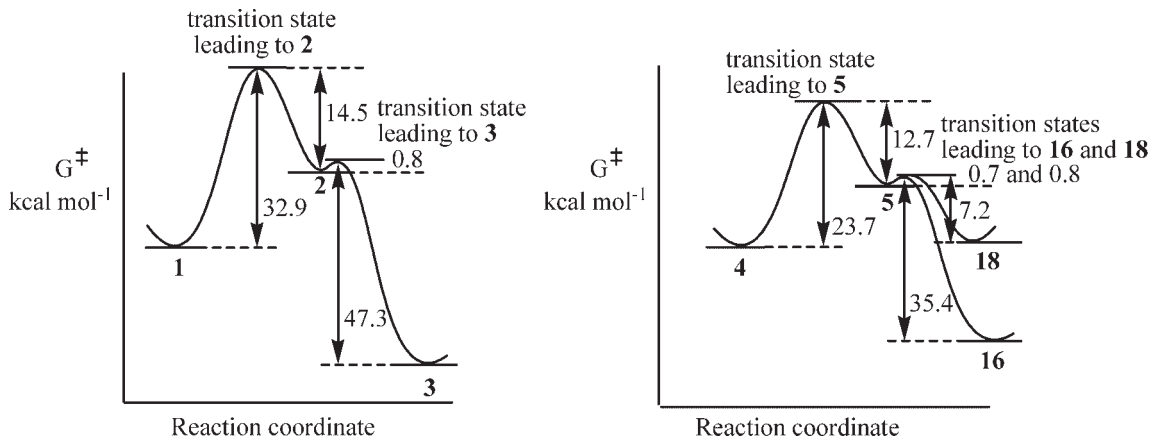

Figure 1. Schematic free energy *versus* reaction coordinate diagrams for thermolysis of **1** and **4**

for $C_6H_{14}NO_4$ $(M+NH_4)^+$ 164.0923 found 164.0881; calcd for $C_6H_{11}O_4$ $(M+H)^+$ 147.0657 found 147.0606.

*Methyl [1-acetoxy-3-hydroxy-1-methyl]diazenecarboxylate (***11***)*

Yellow oil in 7.1% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.67 (s, 3H), 1.99 (s, 1H), 2.06 (s, 3H), 2.17 (t, $J=6.4$ Hz, 2H), 3.72 (t, $J=6.8$ Hz, 2H), 3.94 (s, 3H), although the two CH_2 signals appear to be triplets at 200 MHz, the hydrogens are diastereotopic; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 21.62, 22.29, 40.72, 55.03, 57.39, 102.85, 161.53, 169.22; HRMS (CI, NH_3) *m/z*: calcd for $C_8H_{15}N_2O_5$ $(M+H)^+$ 219.0981 found 219.0977.

Compound **19**

Bicyclic oxadiazoline (49.4 mg, 0.3123 mmol) and DMAD (139.3 mg (99% purity), 0.970 mmol) were placed under nitrogen in a dry ampoule. The mixture was degassed by means of three freeze–pump–thaw cycles and the ampoule was sealed under vacuum. Thermolysis was carried out at 50.0°C for 24 h. The crude product was chromatographed on silica with ether/pentane (1:1) to give 9.40 mg (0.0345 mmol, 11%) of compound **19** as a pale yellow oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ: 1.41 (s, 3H), 2.06 (t, $J=6.3$ Hz, 2H), 3.74 (s, 3H), 3.85 (s, 6H), 4.13 (t, $J=6.4$ Hz, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ: 24.06 (CH_3), 32.11 (C), 36.60 (CH_2), 52.78 (2 OCH_3), 54.74 (OCH_3), 65.40 (OCH_2), 129.15 (2 C═), 155.71 (O_2C═O), 160.21 (2 C═O); IR (Neat, cm^{-1})[14]: 1839, 1751, and 1722; HRMS (CI, NH_3) *m/z*: calcd for $C_{12}H_{17}O_7$ $(M+H)^+$ 273.0975 found 273.0974.

All of the ^{13}C NMR signals were assigned, based on 2D correlation spectra. Gradient HMBC spectra were run in $CDCl_3$ with a Bruker AV 500 instrument.

This paper contains supporting information.

REFERENCES

[1] a) M. El-Saidi, K. Kassam, D. L. Pole, T. Tadey, J. Warkentin, *J. Am. Chem. Soc.* **1992**, *114*, 8751–8752; b) K. Kassam, D. L. Pole, M. El-Saidi, J. Warkentin, *J. Am. Chem. Soc.* **1994**, *116*, 1161–1162. The 100°C rate constant, reported in the reference above, was doubled to estimate the value at 110°C.

[2] P. C. Venneri, J. Warkentin, *Can. J. Chem.* **2000**, *78*, 1194–1203.

[3] G. B. Gubelt, J. Warkentin, *Can. J. Chem.* **1969**, *47*, 3983–3987.

[4] J. Warkentin, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2161–2169 and references cited there.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery,, Jr T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.02 and C.02*, Gaussian, Wallingford, CT, **2004**.

[6] a) O. S. Tee, *J. Am. Chem. Soc.* **1969**, *91*, 7144–7149; b) A. G. Schultz, R. E. Harrington, *J. Org. Chem.* **1991**, *56*, 6391–6394.

[7] P. S. Engel, R. A. Hayes, L. Kiefer, S. Szilagyi, J. W. Timberlake, *J. Am. Chem. Soc.* **1978**, *100*, 1876–1882.

[8] a) D. R. Arnold, L. A. Karnischky, *J. Am. Chem. Soc.* **1970**, *92*, 1404–1406; b) E. A. Curtis, V. P. Sandanayaka, A. Padwa, *Tetrahedron Lett.* **1995**, *36*, 1989–1902; c) J. Bussenius, M. Keller, W. Eberbach, *Liebigs Ann.* **1995**, 1503–1507; d) K. R. Meier, A. Linden, G. Mloston, H. Heimgartner, *Helv. Chim. Acta* **1997**, *80*, 1190–1204.

[9] W. B. Smith, *J. Org. Chem.* **1995**, *60*, 7456–7460.

[10] a) W. Czardybon, A. Klys, J. Warkentin, N. H. Werstiuk, *Can. J. Chem.* **2003**, *81*, 1438–1442; b) A. Klys, W. Czardybon, J. Warkentin, N. H. Werstiuk, *Can. J. Chem.* **2004**, *82*, 1769–1773; c) W. Czardybon, J. Warkentin, N. H. Werstiuk, *J. Org. Chem.* **2005**, *70*, 8431–8436; d) W. Czardybon, J. Warkentin, N. H. Werstiuk, *J. Phys. Org. Chem.* **2005**, *18*, 486–490; e) D. Plazuk, J. Warkentin, N. H. Werstiuk, *Tetrahedron* **2005**, *61*, 5788–5796.

[11] a) T. H. Peterson, B. K. Carpenter, *J. Am. Chem. Soc.* **1992**, *114*, 766; b) C. J. S. M. Simpson, G. J. Wilson, W. Adam, *J. Am. Chem. Soc.* **1991**, *113*, 4728–4732.

[12] M. Dawid, J. Warkentin, *Can. J. Chem.* **2003**, *81*, 598–600.

[13] G. J. Karabatsos, C. E. Osborne, *Tetrahedron* **1968**, *24*, 3361–3368.

[14] S. Han, T. Arrowood, V. G. Young, Jr, S. R. Kass, *Struct. Chem.* **1999**, *10*, 349–354.