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Regio- and Stereoselective Isomerizations of Allenamides: Synthesis of 2-Amido-Dienes and Their Tandem Isomerization-Electrocyclic Ring-Closure

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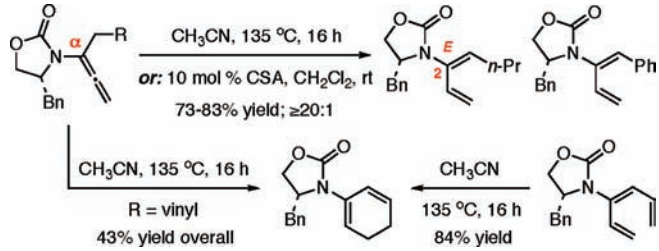
ABSTRACT



A regio- and stereoselective isomerization of allenamides is described, leading to preparations of de novo 2-amido-dienes and a tandem isomerization-6π-electron electrocyclic ring-closure.

Synthesis of conjugated dienes via an allene isomerization, while a thermodynamically favored process, is not trivial kinetically. The required 1,3-H-shift constitutes a four-electron [$2\pi + 2\sigma$] process that would call for an antarafacial approach if proceeding through a concerted and anti-Hückel [or Möbius] transition state.[1,2] Although impossible in an allylic system, it is relatively more feasible for an allenic system because of the presence of orthogonally oriented *p*-orbitals of the *sp*-hybridized central allenic carbon [Scheme 1]. The orthogonal *p*-orbital at C3 [in blue] introduces a formal phase change required for an anti-Hückel transition state, or formally allows a six-electron [$2\pi + 2\sigma + 2\pi$] process when the second set of allenic π-electrons becomes involved. Nevertheless, the calculated[2a] ΔE_{act} value remains high at 77.7 kcal mol^{-1} and consequently, concerted or not, most thermal isomerizations of allenes take place at high temperatures,[3,4] thereby rendering it difficult to control *E*/*Z* ratios of the resulting dienes. There are more practical approaches would involve stepwise processes promoted by acid, base, or metal, but their examples are limited and the level of stereo- and regiochemical control needs to be improved.[3,5]

(1) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1969**, *8*, 781.

(2) (a) Jensen, F. *J. Am. Chem. Soc.* **1995**, *117*, 7487. (b) Lewis, D. K.; Cochran, J. C.; Hossenlopp, J.; Miller, D.; Sweeney, T. *J. Phys. Chem.* **1981**, *85*, 1787.

(3) For general reviews on allenes, see: (a) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004; Vols. 1 and 2.

(4) For some examples, see: (a) Meier, H.; Schmitt, M. *Tetrahedron Lett.* **1989**, 5873. (b) Crandall, J. K.; Paulson, D. R. *J. Am. Chem. Soc.* **1966**, *88*, 4302. (c) Bloch, R.; Perchec, P. L.; Conia, J.-M. *Angew. Chem., Int. Ed.* **1970**, *9*, 798. (d) Jones, M.; Hendrick, M. E.; Hardie, J. A. *J. Org. Chem.* **1971**, *36*, 3061. (e) Patrick, T. B.; Haynie, E. C.; Probat, W. J. *Tetrahedron Lett.* **1971**, *27*, 423. (f) Lehrich, F.; Hopf, H. *Tetrahedron Lett.* **1987**, *28*, 2697.

(5) For some examples, see: (a) Tsuboi, S.; Masuda, T.; Takeda, A. *J. Org. Chem.* **1982**, *47*, 4478. (b) Peng, W.; Zhu, S. *Tetrahedron* **2003**, *59*, 4641. (c) Al-Masum, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3809. (d) Bibas, H.; Koch, R.; Wentrup, C. *J. Org. Chem.* **1998**, *63*, 2619. (e) Jacobs, T. L.; Johnson, R. N. *J. Am. Chem. Soc.* **1960**, *82*, 6397. (f) Buzas, A. K.; Istrate, F. M.; Gagosz, F. *Org. Lett.* **2007**, *9*, 985. (g) Trost, B. M.; Kazmaier, U. *J. Am. Chem. Soc.* **1992**, *114*, 7933. (h) Guo, C.; Lu, X. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1921.

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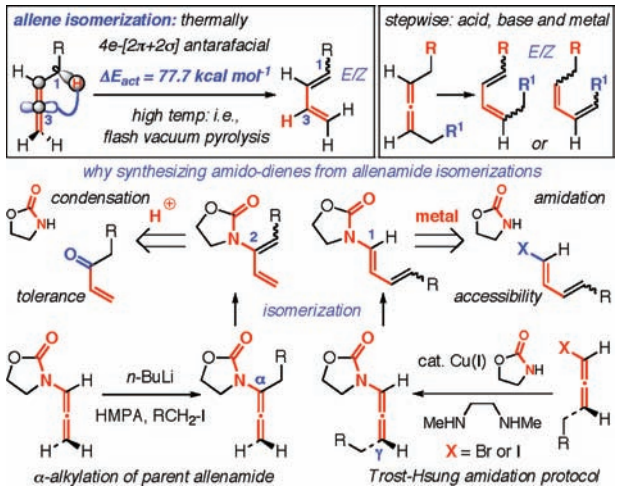
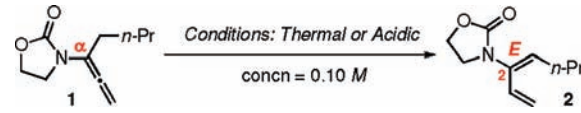
Scheme 1. Allene Isomerizations



Given that most dienes can be prepared from an array of stereoselective transformations, synthesizing conjugated dienes from structurally more challenging allenes through a kinetically demanding and stereochemically undistinguished isomerization does not appear to be a logical first choice. However, our efforts with the chemistry of allenamides[6] allowed us to envision a much greater potential in constructing amido-dienes through isomerizing allenamides[7−9] because there are no consistent approaches for synthesizing amido-dienes.[10−12] Of the two major methods for preparing amido-dienes,[10] the one involving acid-mediated condensations suffers from functional group tolerance with the metal-mediated amidative cross-coupling[13,14] suffering from limited access to halo-dienes [Scheme 1]. In contrast, substituted allenamides are quite accessible through α-alkylations of parent allenamide[15,16] or amidative cross-couplings of allenyl halides.[17] Their isomerizations can prove to be an invaluable entry to amido-dienes. We communicate here a regio- and stereoselective isomerization of allenamides in the synthesis of 2-amido-dienes and a tandem isomerization-6π-electron electrocyclic ring-closure.

Screening through various thermal conditions [entries 1−7 in Table 1] including several solvents distinctly revealed that

Table 1. Thermal vs Acidic Conditions



entry	solvent	acid [10 mol %]	temp [°C]	time [h]	yield [%][a,b]	E:Z[c]
1	CH_3CN	–	25	16	0	–[d]
2	CH_3CN	–	55	16	51	≥20:1
3	CH_3CN	–	85	16	88	≥20:1
4	**CH_3CN**	–	**115**	**16**	**91 [78]**	**16:1**
5	THF	–	115	16	51	9:1
6	$ClCH_2CH_2Cl$	–	115	16	79	7:1
7	Tol	–	150	16	55	4:1
8	CH_2Cl_2	$HNTf_2$	25	5 min	0	–[e]
9	CH_2Cl_2	PTSA	25	1	66	2:1
10	CH_2Cl_2	4-NO_2PhCO_2H	25	16	81	15;1
11	CH_2Cl_2	$PhCO_2H$	25	16	85 [55]	18:1
12	CH_2Cl_2	PPTS	25	16	77	15:1
13	**CH_2Cl_2**	**CSA**	**25**	**10 min**	**95 [74]**	**18:1**

[a] NMR yields. [b] Isolated yields in the bracket. [c] Determined by ^1H NMR. [d] Allenamide **1** was recovered. [e] Allenamide **1** decomposed.

isomerization of achiral allenamide **1** was the most effective at 115 °C in CH_3CN [sealed tube], leading to 2-amido-diene **2**[18] in 78% isolated yield and 16:1 ratio [entry 4] in favor of the *E*-geometry [assigned later]. While there appears to be a solvent effect on the *E/Z* ratio [entries 5−7], we found that with the exception of $HNTf_2$ and PTSA [entries 8−9], a range of Brønsted acids were equally effective and more facile at RT in providing 2-amido-diene **2** with excellent *E/Z* ratio [entries 10−13].

Generality of this α-isomerization could be established as shown in Table 2. Key features are: (1) An array of chiral allenamides **5**−**7** could be employed to construct *de novo* 2-amido-dienes **8**−**10** with comparable yields and *E/Z* ratios under thermal [higher temperature at 135 °C] or acidic conditions [entries 2−11]; (2) unsubstituted 2-amido-dienes **8d** and **9c** could also be accessed in good yields [see R = H in entries 7 and 9]; (3) allenamide **11** containing an acyclic

(6) For a review on allenamide chemistry, see: Hsung, R. P.; Wei, L.-L.; Xiong, H. *Acc. Chem. Res.* **2003**, *36*, 773.

(7) For an earlier example of allenamide isomerizations, see: Overman, L. E.; Clizbe, L. A.; Freerks, R. L.; Marlowe, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 2807.

(8) For a study that likely involved an allenamine intermediate, see: Farmer, M. L.; Billups, W. E.; Greenlee, R. B.; Kurtz, A. N. *J. Org. Chem.* **1966**, *31*, 2885.

(9) For an allenamide isomerization via Grubb's catalyst, see: (a) Kinderman, S. S.; van Maarseveen, J. H.; Schoemaker, H. E.; Hiemstra, H.; Rutjes, F. P. J. T. *Org. Lett.* **2001**, *3*, 2045. (b) Also see ref 17a.

(10) For a review on the synthesis of enamides, see: Tracey, M. R.; Hsung, R. P.; Antoline, J.; Kurtz, K. C. M.; Shen, L.; Slafer, B. W.; Zhang, Y. In *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*; Weinreb, S. M., Ed.; Georg Thieme: Verlag KG, 2005; Chapter 21.4.

(11) For reviews on chemistry of dienamides, see: (a) Overman, L. E. *Acc. Chem. Res.* **1980**, *13*, 218. (b) Petrzilka, M. *Synthesis* **1981**, 753. (c) Campbell, A. L.; Lenz, G. R. *Synthesis* **1987**, 421.

(12) For reviews on chemistry of 2-amino- or 2-amido-dienes: (a) Krohn, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1582. (b) Enders, D.; Meyer, O. *Liebigs Ann.* **1996**, 1023.

(13) For reviews on Cu-mediated C−N and C−O bond formations, see: (a) Lindley, J. *Tetrahedron* **1984**, *40*, 1433. (b) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400. (c) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973. For reviews on Pd-catalyzed *N*-arylations of amines and amides, see: (d) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (e) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. *Acc. Chem. Res.* **1998**, *31*, 805.

(14) For some examples, see: (a) Klapper, A.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7421. (b) Han, C.; Shen, R.; Su, S.; Porco, J. A., Jr. *Org. Lett.* **2004**, *6*, 27. (c) Shen, R.; Lin, C. T.; Bowman, E. J.; Bowman, B. J.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 7889. Also see ref 26b.

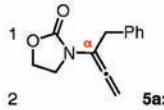
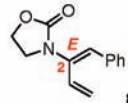
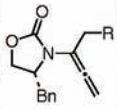
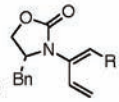
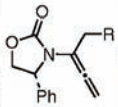
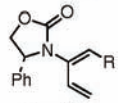
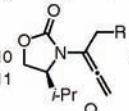
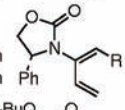
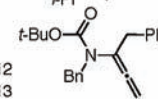
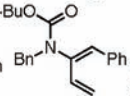
(15) Xiong, H.; Hsung, R. P.; Wei, L.-L.; Berry, C. R.; Mulder, J. A.; Stockwell, B. *Org. Lett.* **2000**, *2*, 2869.

(16) For synthesis of parent allenamides, see: (a) Wei, L.-L.; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* **2001**, *57*, 459.

(17) (a) Trost, B. M.; Stiles, D. T. *Org. Lett.* **2005**, *7*, 2117. (b) Shen, L.; Hsung, R. P.; Zhang, Y.; Antoline, J. E.; Zhang, X. *Org. Lett.* **2005**, *7*, 3081.

(18) See Supporting Information.

Table 2. Isomerization of Allenamides at the α-Position

entry	allenamides	conditions [time][a]	dienes	yield [%][b]	*E*:*Z*[c]
1	 **3**	115 °C, 16 h	 **4**	71	6:1
2	**5a:** R = *n*-Pr	135 °C, 6 h	**8a**	77	≥20:1
3	**5a:** R = *n*-Pr	CSA, 4 h[d]	**8a**	87	≥20:1
4	 **5b:** R = Ph	135 °C, 16 h	 **8b**	74	≥20:1
5	**5b:** R = Ph	CSA, 2 h	**8b**	83	≥20:1
6	**5c:** R = ^{2}Nap	135 °C, 16 h[e]	**8c**	73	≥50:1
7	**5d:** R = H	135 °C, 16 h	**8d**	69	-
7	 **6a:** R = *n*-Pr	CSA, 10 min	 **9a**	82	≥50:1
8	**6b:** R = Ph	CSA, 10 min	**9b**	76	≥50:1
9	**6c:** R = H	135 °C, 16 h	**9c**	69	-
10	 **7a:** R = *n*-Pr	135 °C, 16 h	 **10a**	62	≥50:1
11	**7b:** R = Ph	135 °C, 16 h	**10b**	82	≥50:1
12	 **11**	135 °C, 16 h	 **12**	45	≥20:1
13	**11**	CSA,[f] 2 h	**12**	61	≥20:1

[a] Unless otherwise noted, CH_3CN was the solvent for thermal conditions, and CH_2Cl_2 was the solvent when using 10 mol % of CSA at rt. For all reactions, concn = 0.10 M. [b] Isolated yields. [c] Determined by ^{1}H NMR. [d] Temp started at −78 °C. [e] $ClCH_2CH_2Cl$ was used. [f] MS (4 Å) was used.

amide is also feasible for the isomerization; and (4) a single-crystal X-ray structure of **10b** was attained to unambiguously assign the *E*-configuration [Figure 1].

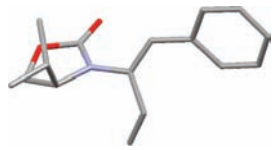


Figure 1. X-ray structure of 2-amido-diene **10b**.

Although our main interest resides in identifying a useful protocol for synthesizing 2-amido-dienes given its greater scarcity,[10−12,19,20] we examined isomerizations of allenamides from the γ-position en route to more well-known 1-amido-dienes.[21] As shown in Table 3, isomerizations of two types of γ-substituted allenamides, those with a cyclohexylidene group [see **13**−**16** in entries 1−13], and those with an isopropylidene group [see **17**−**19** in entries 14−19] led to 1-amido-dienes **20**−**26** exclusively as *E*-enamides [assigned based on the *trans*-olefinic proton coupling constant].

(19) For leading examples of 2-amido-dienes, see: (a) Ha, J. D.; Kang, C. H.; Belmore, K. A.; Cha, J. K. *J. Org. Chem.* **1998**, *63*, 3810. (b) González-Romero, C.; Bernal, P.; Jiménez, F.; Cruz, M. C.; Fuentes-Benites, A.; Benavides, A.; Bautista, R.; Tamariz, J. *Pure Appl. Chem.* **2007**, *79*, 181, and references cited therein. (c) Movassaghi, M.; Hunt, D. K.; Tjandra, M. *J. Am. Chem. Soc.* **2006**, *128*, 8126.

(20) For some examples of 2-amino-dienes, see: (a) Enders, D.; Meyer, O.; Raabe, G. *Synthesis* **1992**, 1242. (b) Barluenga, J.; Canteli, R.-M.; Flrez, J.; Garca-Granda, S.; Gutirrez-Rodrguez, A.; Martín, E. *J. Am. Chem. Soc.* **1998**, *120*, 2514.

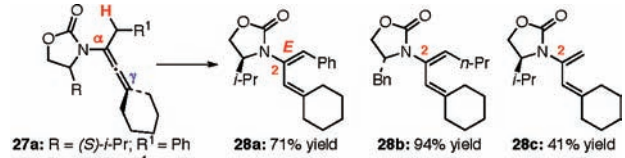
Table 3. Isomerization of Allenamides at the γ-Position

entry	allenamides	conditions [time][a]	dienes	yield [%][b,c]
1	**13a:** R = *(R)*-Ph	135 °C, 16 h	**20a**	≤10[d]
2		PTSA, 10 min		95
3		CSA, 10 min		89
4	**13b:** R = *(R)*-Bn	135 °C, 16 h	**20b**	25[e]
5		PTSA, 5 min		96
6		CSA, 10 min		95
7	**13c:** R = *(S)*-*i*-Pr	135 °C, 16 h[e]	**20c**	50[f]
8		PTSA, 10 min		88
9	**14:** W = Ac; R = Ph	175 °C,[g] 24 h	**21**	95
10		CSA,[h] 10 min		90
11	**15:** W = Ts; R = Bn	175 °C,[g] 24 h	**22**	96
12		CSA,[h] 10 min		97
13	**16:** W = $PhCH_2CH_2CO$, R = Ph	175 °C,[g] 24 h	**23**	98
14	**17**	135 °C, 16 h	**24**	95
15	**17**	PTSA, 5 min	**24**	⌟
16	**18:** W = Ac; R = Ph	175 °C,[g] 24 h	**25**	46[i]
17		CSA,[h] 10 min		97
18	**19:** W = Ts; R = Bn	135 °C, 48 h	**26**	77[j]
19		CSA,[h] 10 min		99

[a] Unless otherwise noted, CH_3CN was the solvent for thermal conditions, and CH_2Cl_2 was the solvent when using 10 mol % of PTSA or CSA at rt. In all reactions, concn was 0.10 M. [b] Isolated yields. [c] Only *E* isomers were observed. [d] Ninety percent starting allenamide recovered. [e] Seventy percent starting allenamide recovered. [f] Forty-four percent starting allenamide recovered. [g] Toluene was the solvent. [h] MS (4 Å) was used. [i] Decomposition. [j] NMR yields.

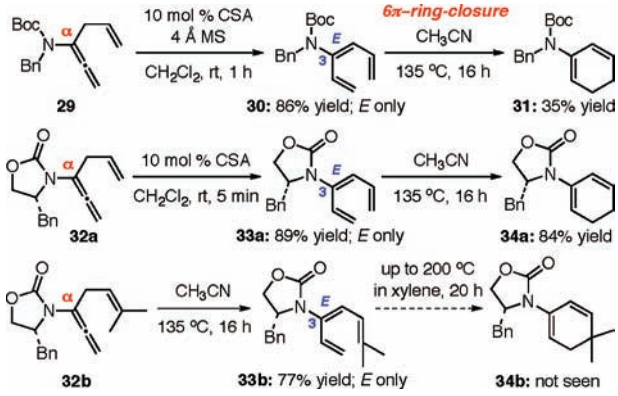
A keen observation here for the γ-isomerization is that acidic conditions appear to be more effective in general with the exception of **17** [entry 15]. In addition, thermal isomerizations at the γ-position required higher temperatures and/or longer reaction times than those of α-isomerizations. This difference prompted us to explore a possible regioselective isomerization. As shown in Scheme 2, when heating allenamides **27a** and **27b**, containing both α- and γ-substituents, at 135 °C in CH_3CN, isomerizations occurred exclusively at the α-position, leading to 2-amido-dienes **28a** and **28b**[22] in 71 and 94% yields, respectively, all in favor of the *E*-enamide [assigned by NOE[18]]. Isomerization of allenamide **27c** took place at RT when in contact with silica gel but again α-isomerization was favored. This regioselective isomerization are both mechanistically intriguing[23] and should be great synthetic value in constructing highly substituted 2-amido-dienes.

Scheme 2. Regioselective α-Isomerizations



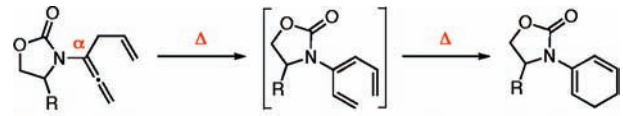
The *E*-selectivity[23] attained from α-isomerization provides an excellent platform for the following important pericyclic transformation. As shown in Scheme 3, isomerization of α-allylated allenamide **29** under acidic conditions afforded 3-amido-triene **30** in 86% yield. With the *E*-selectivity, triene **30** is perfectly suited for a thermal 6π-electron electrocyclic ring-closure[24] to give cyclic diene **31**. Although only in 35% yield,[25] examples of cyclic 2-amido-dienes such as **31** are more rare.[26] Allenamide **32a** provided a good example of synthesizing cyclic 2-amido-diene **34a** via acid-promoted α-isomerization followed by ring-closure. Allenamide **32b** demonstrated that the thermal isomerization could be arrested with the *gem*-dimethyl group in triene **33b** impeding the ring-closure. Unfortunatedly, attempted ring-closure of **32b** at 200 °C led to an unidentified product instead of **34b**.

Scheme 3. 3-Amido-Trienes and Pericyclic Ring-Closure



At last, this process could be rendered in tandem under thermal conditions to access cyclic 2-amido-dienes **34a**, **37**, and **38** in good overall yields directly from respective allenamides **32a**, **35**, and **36** [Scheme 4]. It is noteworthy that these 6π-electron pericyclic ring-closures mostly took place at 135 °C, which implies an accelerated process. This feature is consistent with related ring-closures of 1,3,5-hexatrienes bearing a C3-donating group.[27,28]

Scheme 4. Tandem α-Isomerization-Pericyclic Ring-Closure



We have described here a regio- and stereoselective isomerization of allenamides, leading to preparations of *de novo* 2-amido-dienes and a tandem isomerization-6π-electron electrocyclic ring-closure. Studies involving applications of these dienes and this new tandem process as well as mechanistic understanding of this allene-isomerization are underway.

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Supporting Information Available: Experimental procedures as well as NMR spectra, characterizations, and X-ray structural files are available for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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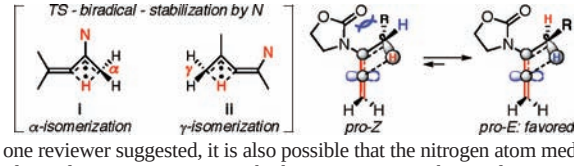
(21) For examples, see: (a) Terada, A.; Murata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1644. (b) Overman, L. E.; Clizbe, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 2352. (c) Oppolzer, W.; Bieber, L.; Francotte, E. *Tetrahedron Lett.* **1979**, 4537. (d) Smith, A. B., III.; Wexler, B. A.; Tu, C.-Y.; Konopelski, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1308. (e) Schlessinger, R. H.; Pettus, T. R. R.; Springer, J. P.; Hoogsteen, K. *J. Org. Chem.* **1994**, *59*, 3246. (f) Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **1997**, *119*, 7165. (g) Huang, Y.; Iwama, T.; Rawal, V. H. *J. Am. Chem. Soc.* **2002**, *124*, 5950. (h) Robiette, R.; Cheboub-Benchaba, K.; Peeters, D.; Marchand-Brynaert, J. *J. Org. Chem.* **2003**, *68*, 9809.

(22) There appears to be ~5% of 1-amido-diene from γ-isomerization.

(23) Without detailed studies, a rationale for lowering of the thermal activation barrier of 1,3-H-shift is the stabilization of the bi-radical intermediate provided by the nitrogen atom, assuming a radical intermediate is considered electron deficient. Based on the this model, this stabilization is direct when isomerizations take place at the α-position [see **i**], and "vinylogous" for isomerizations at the γ-position [see **ii**]. Thus, thermal isomerizations at the α-position were faster than at the γ-position.



As one reviewer suggested, it is also possible that the nitrogen atom mediates a polarized transition sate in which an increasing charge density at the β-carbon could develop, leading to an N-acyl iminium ion-like character with the migrating hydrogen behaving more like a proton. This charged transition state instead of a neutral one should possess a lower thermal activation barrier for the 1,3-H-shift. Finally, a rationale for the E-selectivity from the thermal α-isomerization is that the *pro-Z*-TS experiences a greater allylic strain than the *pro-E*-TS during the 1,3-H-shift, although we cannot rule out equilibration from *Z*- to *E*-enamide after the initial isomerization.

(24) For reviews for pericyclic ring-closures, see: (a) Marvell, E. N. *Thermal Electrocyclic Reactions*, Academic Press: New York, 1980. (b) Okamura, W. H.; de Lera, A. R. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: New York, 1991; Vol. 5, pp 699−750. For reviews on ring-closure in natural product synthesis, see (c) Pindur, U.; Schneider, G. H. *Chem. Soc. Rev.* **1994**, 409. (d) Beaudry, C. M.; Malerich, J. P.; Trauner, D. *Chem. Rev.* **2005**, *105*, 4757.

(25) When attempting the ring-closure at temperature ≥180 °C, diene **30** slowly isomerized to the respective 1-amido diene.

(26) For examples, see: (a) Martínez, R.; Jiménez-Vázquez, H. A.; Delgado, F.; Tamariz, J. *Tetrahedron* **2003**, *59*, 481. (b) Wallace, D. J.; Klauber, D. J.; Chen, C. Y.; Volante, R. P. *Org. Chem.* **2003**, *5*, 4749. (c) Wabnitz, T. C.; Yu, J.-Q.; Spencer, J. B. *Chem.−Eur. J.* **2004**, *10*, 484.

(27) For theoretical studies on substituent effects on electrocyclic ring-closure of 1,3,5-hexatrienes, see: (a) Spangler, C. W.; Jondahl, T. P.; Spangler, B. *J. Org. Chem.* **1973**, *38*, 2478. (b) Guner, V. A.; Houk, K. N.; Davies, I. A. *J. Org. Chem.* **2004**, *69*, 8024. (c) Yu, T.-Q.; Fu, Y.; Liu, L.; Guo, G. X. *J. Org. Chem.* **2006**, *71*, 6157. (d) Duncan, J. A.; Calkins, D. E. G.; Chavarha, M. *J. Am. Chem. Soc.* **2008**, *130*, 6740.

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