Lanthanide- and DMSO-Induced Ring Opening of 2-Iminooxetanes: Synthesis of β-Lactams and β-Keto Amides

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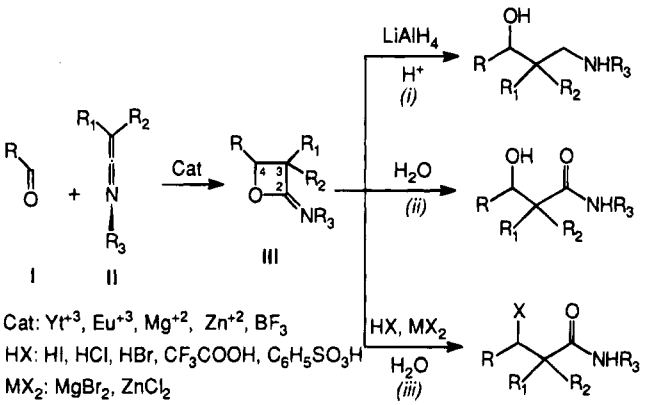
2-Iminooxetanes (**1**), generated by lanthanide-catalyzed heterocycloaddition of aldehydes to ketene imines, are versatile synthons for β-lactams (**2**) and for β-keto amides (**3**). Conversion of **1** into **2** and **3** can be accomplished by either lanthanide-induced or oxidative (DMSO) ring opening, respectively.

Introduction

We have been interested for some time in the synthesis and reactivity of four-membered-ring heterocycles for the development of synthetic routes to highly functionalized starting materials. In an exploratory investigation[1] we showed that 2-iminooxetanes, by virtue of their reactivity, are valuable synthetic intermediates that can be used for the introduction of C2, C3, and C4 units into organic compounds. For this reason we developed a new strategy for the synthesis of 2-iminooxetanes that have diverse functionality at C3 and C4 via lanthanide-induced [2 + 2]-heterocycloaddition[2] of aldehydes to ketene imines (Scheme 1). This investigation evolved into a detailed study of a variety of ring-opening reactions. In particular, (i) the reduction of 2-iminooxetanes with $LiAlH_4$ afforded γ-amino alcohols[3] and (ii) the hydrolysis of 2-iminooxetanes, catalyzed by trace amounts of sulfuric acid, yielded the corresponding β-hydroxy amides.[4] Interestingly, 2-iminooxetanes can be considered as valence isomers of β-lactams. We have recently demonstrated that *trans* and *cis* C3,C4-monosubstituted 2-iminooxetanes represent important starting materials for the stereoselective synthesis of β-lactams. In fact, the electrophilically initiated ring opening (iii) of *trans*- and *cis*-2-iminooxetanes, in the presence of appropriate electrophile–nucleophile combinations (HI, CF_3COOH, $C_6H_5SO_3H$, etc.), led to the corresponding *erythro*- and *threo*-β-substituted propionamides,[5] respectively, and the base-induced N–C3 ring closure of these intermediates afforded the corresponding *trans*- and *cis*-β-lactams, respectively.[5,6] Next, we thought it might be possible to synthesize β-lactams directly via isomerization of the 2-iminooxetanes in a one-pot procedure. The literature reports the isomerization of a 2-iminiooxetane, derived from the photocycloaddition of diphenyl-*N*-phenylketene imine and fluorenone anil, into the corresponding β-lactam when isolation by Florisil chromatography was attempted.[7] By contrast, our attempts to perform the isomerization of a selected number of oxetanes (**1a**, **1b**, **1f**, and **1g** of Scheme 2) using this method failed. This paper focuses on our preliminary attempts to facilitate the isomerization process by performing the thermolysis under different conditions.

Scheme 1



Results and Discussion

Ring Opening of 2-Iminooxetanes in a Neat State. 2-Iminooxetanes are in general sensitive to silica gel. Such acidity favors an uncontrolled partial hydrolysis of the oxetanes leading to the corresponding β-hydroxy amides. In several cases this undesired side reaction was avoided with carefully dried solvents and silica preheated in an oven (120 °C, 1 day). Once isolated in a pure state, 2-iminooxetanes were fairly stable upon heating; an uncontrolled decomposition leading to tarry material occurred at temperatures >200 °C. When a 2–4% amount of a lanthanide shift reagent[8] was admixed with the oxetanes in a neat state (see Experimental Section), the ring opening occurred at lower temperatures, and the corresponding β-lactams were obtained as the major products. Table 1 reports the results of the isomerization process of a number of C3-disubstituted (**1a–e**) and C3-monosubstituted (**1f–i**) 2-iminooxetanes in the presence of $Yb(FOD)_3$, $Yb(HFC)_3$, and $Eu(HFC)_3$. The isomerization occurs with different types of substituents at C4, such as aliphatic (**1b**, **1g**, **1h**, and **1i**), aromatic (**1a**, **1e**), and heteroaromatic (**1d**), and with vinyl substituents at both C4 and C3 (**1c**, **1e**). It is worth noting that the vinyl substituent at C4 can produce an alternative pericyclic pattern, which can give, in principle, a less strained six-

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(1) Barbaro, G.; Battaglia, A.; Giorgianni, P. *Tetrahedron Lett* **1987**, *26*, 2995.

(2) Barbaro, G.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1988**, *53*, 5501. Barbaro, G.; Battaglia, A.; Giacomini, D.; Giorgianni, P. *Tetrahedron* **1993**, *49*, 4293.

(3) Barbaro, G.; Battaglia, A.; Giorgianni, P. Unpublished results. See also ref 1.

(4) Barbaro, G.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1992**, *57*, 5128.

(5) Barbaro, G.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1994**, *59*, 906.

(6) See for example: Bose, A. K.; Saha, D. P.; Manhas, M. S. *J. Org. Chem.* **1981**, *46*, 1229.

(7) Singer, L. A.; Davis, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 941.

(8) The lanthanides used were tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium [$Yb(fod)_3$]; tris[(heptafluoroprop-3-yl)hydroxymethylene]-(+)-camphoratolytterbium, and europium [$Yb(hfc)_3$ or $Eu(hfc)_3$].

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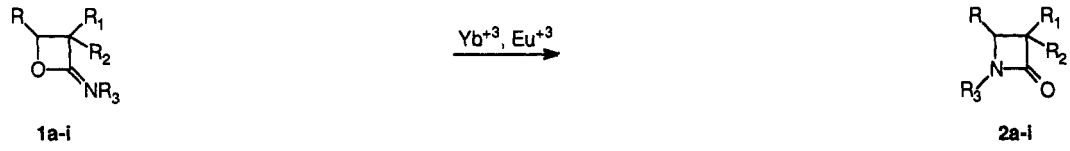
Scheme 2

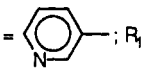


1a-i **2a-i**

1a, 2a: R = C_6H_5; R_1 = R_2 = Me, R_3 = Tol

1b, 2b: R = Me_2CH; R_1 = R_2 = Me, R_3 = Tol

1c, 2c: R = CH_2=CH; R_1 = R_2 = Me, R_3 = Tol

1d, 2d: R =  ; R_1 = R_2 = Me, R_3 = Tol

1e, 2e: R = C_6H_5; R_1 = Me, R_2 = CH_2=CH, R_3 = Tol

1f, 2f: R = H; R_1 = Me, R_2 = H, R_3 = An

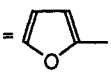
1g, 2g: R = Me_2CH; R_1 = Me, R_2 = H, R_3 = Tol

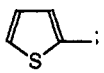
Tol = C_6H_4-*p*-Me; An = C_6H_4-*p*-OMe

1h, 2h: R = $MeCH_2CH_2$-; R_1 = Me, R_2 = H, R_3 = An

1l, 2l: R = Me-C≡C; R_1 = Me, R_2 = H, R_3 = An

1l, 2l: R = CO_2Me; R_1 = Me, R_2 = H, R_3 = Tol

1m, 2m: R =  ; R_1 = Me, R_2 = H, R_3 = An

1n, 2n: R =  ; R_1 = Me, R_2 = H, R_3 = An

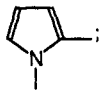
1o, 2o: R =  ; R_1 = Me, R_2 = H, R_3 = An

Table 1. Synthesis of β-Lactams by Lanthanide-Induced Ring Isomerization of 2-Iminooxetanes in a Neat State

entry	reagent	catalyst	T, °C	t, min	yield of product (%)	ratio[a] of *cis*:*trans*
1	**1a**	Yb(HFC)$_3$[c]	160	30	**2a** (78)	
2	**1b**	Yb(HFC)$_3$[d]	175	50	**2b** (75)	
3	**1c**	Yb(HFC)$_3$[c]	170	30	**2c** (77)	
4	**1d**	Yb(HFC)$_3$[c]	125	25	**2d** (38)	
5	*cis*-**1e**	Yb(FOD)$_3$[c]	150	25	**2e** (51)	30:20
6	*trans*-**1e**	Yb(FOD)$_3$[c]	150	25	**2e** (56)	23:33
7	**1f**	Eu(HFC)$_3$[c]	130	30	**2f** (65)	
8	*trans*-**1g**	Yb(HFC)$_3$[d]	200	120	**2g** (36)	*trans*
9	*cis*-**1g**	Yb(HFC)$_3$[d]	200	120	**2g** (37)	30:7
10	**1h**[b]	Eu(HFC)$_3$[d]	200	90	**2h** (48)	20:28
11	*cis*-**1i**	Yb(FOD)$_3$[d]	100	600	**2i** (42)	38:4

[a] Determined from the proton ratios in the ^{1}H NMR. [b] *trans*/*cis* = 1.28. [c] 2.0 molar % with respect to the reagent. [d] 4.0 molar % with respect to the reagent.

membered heterocycle. However, we could not detect the presence of such an isomer in the crude reaction mixture.

Yields of the corresponding β-lactams were moderate to good, ranging between 36% (*trans*-**1g**) and 78% (**1a**). There are several reasons for the loss of product. Decomposition of the 2-iminooxetanes or of the β-lactams leading to tarry material was observed mainly during the isomerization of compounds **1d** and **1e**. For this reason we studied the stability of β-lactams **2d** and **2e** upon heating. A 1:1 *cis*/*trans* mixture of β-lactams **2e** was recovered in 92% yield (*cis*/*trans* = 1:1) after 40 min at 150 °C and in the presence of 2 molar % of Yb(FOD)$_3$. In contrast, β-lactam **2d** was recovered in 58% yield after 30 min at 125 °C in the presence of 2 molar % of Yb(HFC)$_3$. These results suggest that the formation of tarry material observed in the isomerization of *cis*- and *trans*-**1e** is mainly due to decomposition of the reagents, whereas in the isomerization of **1d** it is due to decomposition of both reagents and products. Moreover, uncontrolled side reactions always occurred. In fact, an inspection of the crude reaction mixture by IR spectroscopy revealed the formation of trace amounts of isocyanates and of alkenes, deriving from a cycloreversion of the oxetanes and/or of the β-lactams along the *Y* axis (Chart 1). Finally, minor amounts of α,β-unsaturated amides of general formula RCH=CMeCONHR$_3$ were also obtained as side products arising from ring opening of C3-methyl monosubstituted oxetanes **1f–i**. These amides were not formed by decomposition of the products. Actually, β-lactams **1f**, **1g**, and **1h** were stable under the

Chart 1

Chart 2

trans-**1e** *cis*-**1e**

reaction conditions (see Experimental Section), with only minor amounts (<18%) of tarry material being formed. Alternatively, the α,β-unsaturated amides could be formed via a hydrolytic ring opening of the 2-iminooxetanes, leading to the corresponding β-hydroxy amides (e.g., Scheme 1, path ii), and subsequent dehydration. We believe this alternative to be unlikely, since the formation of β-hydroxy amides requires the presence of water in the reaction mixture[5] and the isomerization experiments were performed on pure compounds, in sealed vials, and under anhydrous conditions. Moreover, attempts to obtain α,β-unsaturated amides from the dehydration of the *erythro* and *threo* β-hydroxy amides of 2-iminooxetanes **1g** and **1h**[5] failed. This result suggests that amides were probably formed via a C4–O ring opening of the reagents followed by 1,3-H migration of the hydrogen atom at C3 to the nitrogen atom.

The isomerization of *cis* and *trans* C3-disubstituted oxetanes **1e** (Chart 2) and of *cis* and *trans* C3-methyl-monosubstituted oxetanes **1g–i** produced diastereomeric mixtures of the corresponding *cis* and *trans* β-lactams **2e** and **2g–i**. In the case of compounds **2e** the assignment of *cis*/*trans* configuration was based on the assumption that the methyl group at C3 of the isomer *trans* isomer is at higher field than that of *cis* because of the upfield effect exerted by its syn vicinal phenyl substituent.[9] The *cis*/*trans* stereoconfigurational assignments of **2h** and **2i**, together with the criteria used for **2g**, are reported elsewhere.[5] It is worth noting that the reaction of diastereomerically pure *cis* and *trans* oxetanes **1e** took

(9) This criterion was also used for the *cis*/*trans* (*Z*/*E*) stereoconfigurational assignment of the corresponding 2-iminooxetanes *cis*- and *trans*-**1e**. See ref 2.

Scheme 3

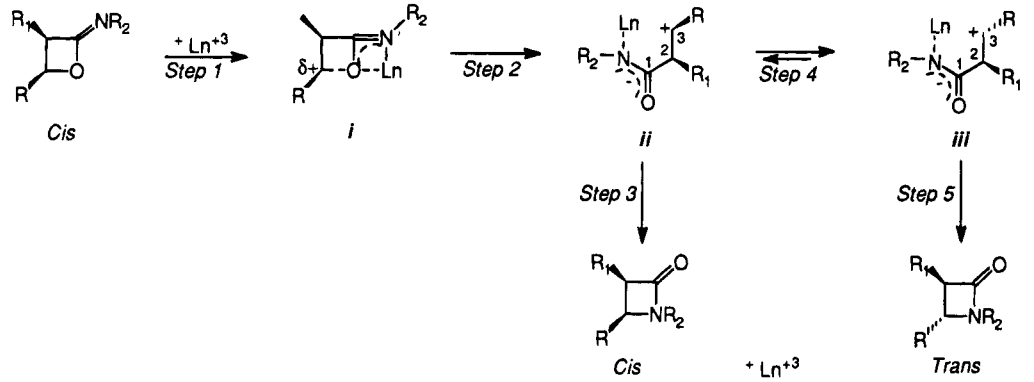


Table 2. Synthesis of β-Lactams by Ring Isomerization of 2-Iminooxetanes in HMPA

entry	reagent	catalyst (mmol %)	T, °C	t, min	yield of product (%)	ratio[a] of cis:trans
1	*cis*-**1h**	Eu(HFC)$_3$ (3)	150	45	**2h** (25)	*cis*
2	*trans*-**1h**	Eu(HFC)$_3$ (3)	140	150	**2h** (37)	*trans*
3	*cis*-**1i**	Yb(FOD)$_3$ (3)	75	200	**2i** (28)	*cis*
4	*trans*-**1i**	Yb(FOD)$_3$ (4)	75	200	**2i** (24)	5:19
5	*cis*-**1l**	Eu(HFC)$_3$ (2)	130	120	**2l** (45)	37:8
6	*trans*-**1l**		130	90	**2l** (42)	*trans*
7	*trans*-**1l**	Eu(HFC)$_3$ (2)	130	25	**2l** (62)	*trans*
8	**1d**		130	120	**2d** (45)	

[a] Determined from the proton ratios of ^{1}H NMR.

Table 3. Synthesis of β-Lactams by Lanthanide-Induced Ring Isomerization of 2-Iminooxetanes in CCl_4 Solutions

entry	reagent	catalyst[a]	T, °C	t, min	yield of product (%)	ratio[b] of cis:trans
1	**1m**[c]	Yb(FOD)$_3$	25	50	**2m** (31)	11:20
2	**1n**[d]	Yb(FOD)$_3$	25	50	**2n** (31)	10:21
3	**1o**[e]	Yb(FOD)$_3$	40	150	**2o** (33)	10:23

[a] 1.5 mol % with respect to the ketene imine. [b] Determined from the proton ratios of ^{1}H NMR. [c] *trans/cis* = 0.67 at 80% of conversion of the corresponding ketene imine. [d] *trans/cis* = 0.5 at 70% conversion of the corresponding ketene imine. [e] *trans/cis* ratio not determined.

place with substantial stereochemical scrambling, the product of retention being obtained primarily.

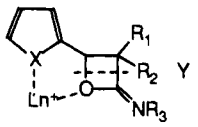
Ring Opening of 2-Iminooxetanes in HMPA Solutions. The possibility of improving the yields of the lactim-to-lactam conversion in the reactions of C3,C4-monosubstituted oxetanes was explored by performing the reactions in a solvent. The reactions of oxetanes **1a** and **1h** in refluxing *p*-xylene and in the presence of 4 molar % of Eu(HFC)$_3$ or Yb(HFC)$_3$ as catalysts failed to give the corresponding β-lactams. Instead, the isomerization of a number of 2-iminooxetanes (**1d**, **1h**, **1i**, and **1l**, Table 2) was successfully achieved when the strongly polar HMPA was used as the solvent. It is worth noting that the HMPA-induced ring isomerization of *cis/trans* C4-alkyl substituted oxetanes **1h** and **1i** (entries 1–4, Table 2) occurred at a temperature lower than that used in the reactions performed in a neat state (entries 10 and 11, Table 1), but the yields of the corresponding β-lactams were significantly lowered probably because HMPA also favored the above-mentioned side reactions. In addition, the lactim-to-lactam isomerization of oxetanes bearing electron-acceptor substituents at C4, such as the pyridin-3-yl (**1d**) and the CO_2Me (*trans*-**1l**) derivatives (entries 6 and 8, Table 2), occurred even in the absence of the lanthanide catalyst irrespective of mono- or disubstitution at C3. However, the addition of Eu(HFC)$_3$ to an HMPA solution of *trans*-**1l** increased the reactivity and the yield of β-lactam (entry 7), thus demonstrating the efficiency of the lanthanide catalyst even in the presence of this polar solvent.

The results listed in Tables 1 and 2 show that the ring isomerization of *trans* C3-methyl-monosubstituted oxetanes **1g–l** occurred with high diastereocontrol. The stereochemical course of this transformation favored retention of configuration. Only compound *trans*-**1i** gave minor amounts of inversion product. Some stereochemical scrambling was generally observed in the isomerization of the corresponding *cis* isomers, the retention product being, however, the major isomer.

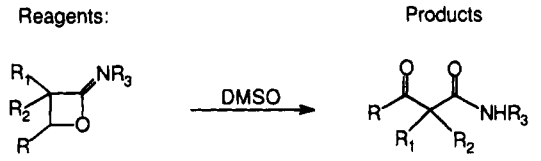
Ring Opening of 2-Iminooxetanes Bearing a Five-Membered Ring Heterocycle at C4. 2-Iminooxetanes **1m-o**, bearing a five-membered ring heterocycle at the C4 carbon atom, showed interesting behavior. In fact, the presence of 2-yl heteroatom (O, S, NMe) favors both the lactim-to-lactam isomerization and the concurrent cycloreversion, which affords the corresponding isocyanate and alkene (see Experimental Section and Table 3), at relatively low temperatures (25–40 °C). The formation of these byproducts raises the question of the mechanism of the lactim-to-lactam isomerization. The formation of the β-lactams could be explained by a lanthanide-induced cycloaddition of the isocyanates and alkenes after they were formed. To test this hypothesis, we attempted control experiments to synthesize the β-lactams via lanthanide-induced cycloaddition of the isocyanates and alkenes obtained from the cycloreversion of **1a**, **1m**, and **1n**. Only a thermal- and/or a lanthanide-induced formation of oligomers from the isocyanates was observed.

Alternatively, the isomerization may involve the formation of carbocation **ii**, via ring opening of the C–O bond of complex **i** (Scheme 3) of the oxetane and the positive fragment of the Lewis acid, and subsequent N–C3 ring closure. The formation of the retention product involves a frontside nucleophilic attack of the nitrogen atom at the C3 carbon atom prior to rotation around the C2–C3 bond (step 3). The partial stereochemical scrambling may be explained by a rotation around to the C2–C3 bond (step 4) before the N–C3 ring closure (step 5). This mechanism parallels that of the addition of acids to 2-iminooxetanes,[5] the type of product being dependent on appropriate electrophile–nucleophile combinations in the structure of the Lewis acid. In both cases the oxophilicity of the positive fragment of the Lewis acid (Yb^{+3}, Eu^{+3}, Mg^{+2}, H^+, etc.) is responsible for the ring opening, and the conjugate base of the Lewis acid is responsible for the type of product. Namely, nucleophilic counterions give rise to β-substituted propionamides, whereas very weak nucleophilic partners,

Chart 3



Scheme 4



1p, 3p: R=CH_2=CH, R_1 = R_2 = Me, R_3 = Mes
1q, 3q: R=C_6H_5, R_1 = H, R_2 = Me, R_3 = Mes
1r, 3r: R = 3-Pyrido, R_1 = H, R_2 = Me, R_3 = An

such as 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato (FOD) or (heptafluoroprop-3-yl)hydroxymethylene)-(+)-camphorato (HFC) ligands, favor the formation of intermediate carbocation **ii** of Scheme 3 and the subsequent N−C3 ring closure. The smooth pyrolysis of oxetanes **1m−o** could be tentatively explained by the formation of a strong five-membered chelate, involving the 2-yl heteroatom, the lanthanide, and the oxygen atom of the oxetane, which favors bond breaking at C−O (Chart 3). This proposal is supported by the higher reactivity of the furan derivative due to the formation of a stronger chelate between the oxophilic ytterbium atom and 2-yl oxygen of the furan with respect to the sulfur or nitrogen atoms of the 4-thiophene-2-yl and of the 4-*N*-methylpyrrole-2-yl derivatives.

Ring Opening of 2-Iminooxetanes in DMSO: Formation of β-Keto Amides. The ring opening of 2-iminooxetanes in DMSO is discussed in a separate section, since DMSO induced an oxidative ring opening leading to the formation of the corresponding β-keto amides, instead of the expected ring isomerization (Scheme 4). This result is not unexpected, since DMSO has been used in a variety of oxidation reactions.[10] In our case the oxidation of a selected number of 2-iminooxetanes (Table 4) occurred at 130−150 °C under neutral conditions, the corresponding β-keto amides being formed in good to high yields. A possible mechanism for the oxidative ring opening is depicted in Scheme 5. Nucleophilic attack of the oxygen atom of DMSO at the C4 carbon atom of the oxetane causes the ring opening, favoring the formation of a zwitterionic intermediate. Elimination of Me_2S and migration of the C3-*H* hydrogen atom to the nitrogen atom affords the corresponding amide.

Conclusions

This study has brought to light an interesting application of lanthanides in organic synthesis. In fact, many protocols dealing with the utilization of lanthanide reagents for simple functional group transformations (for example, oxidation and reduction processes) or with the application of lanthanides in selective carbon−carbon bond forming reactions have been developed in the last few years.[11] However, to our knowledge, nothing has been reported in the literature on the possibility of employing the strong oxophilicity of lanthanides to induce a lactim-to-lactam interconversion in heterocycles. However, a similar lanthanide-induced isomerization has been observed in a six-membered ring heterocycle.[2] In the series of four-membered ring heterocycles, our study demonstrates that the lanthanide-induced ring opening of 2-iminooxetanes outlines an original approach to the synthesis of β-lactams and at the same time demonstrates that the synthesis of 2-iminooxetanes and their isomerization can be performed in one pot, since both reactions may be induced by the same catalyst. At the present time, the 2-iminooxetanes bearing two substituents at C3 seem to give higher yields of β-lactam when compared with monosubstituted analogs. Probably, the disubstitution at C3 causes steric congestion that favors ring opening, and, at the same time, prevents the concurrent 1,3-hydrogen shift that leads to α,β-unsaturated amides.[12]

Table 4. Synthesis of β-Keto Amides by DMSO-Induces Ring Opening of 2-Iminooxetanes

entry	reagent	*trans/cis*	*T*, °C	*t*, min	product	yield, %
1	**1a**		140	300	**3a**	85
2	**1b**		150	360	**3b**	77
3	**1e**	0.2	150	30	**3e**	76
4	**1g**	1.3	140	50	**3g**	64
5	**1h**	1.2	150	60	**3h**	53
6	**1p**		140	30	**3p**	70
7	**1q**	1.0	130	180	**3q**	76
8	**1r**	1.2	140	30	**3r**	69

Experimental Section

General. IR spectra were obtained from CCl_4 solutions. Mass spectra were recorded at an ionizing voltage of 70 eV. All the solvents were dried and purified by means of standard procedures.

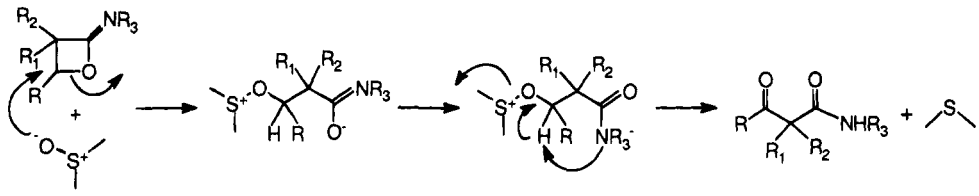
Starting Materials. The 2-iminooxetanes were prepared from the corresponding aldehydes and ketene imines by means of literature procedures.[2,3]

General Procedure for the Synthesis of β-Lactams in a Neat State. The 2-iminooxetanes and the catalyst, dissolved in 2−3 mL of CH_2Cl_2, were introduced into a vial under argon. The vial was sealed after the solvent was removed under vacuum, and the contents were heated at the selected temperature for the time required. The *cis/trans* isomer distribution of β-lactams **2** was evaluated directly on the crude product material by ^1H NMR spectroscopy.

General Procedure for the Synthesis of β-Lactams in Solution. The 2-iminooxetanes, the catalyst, and the solvent were introduced into a vial under argon. The vial was sealed and heated at the selected temperature for the time required. The solvent was removed under vacuum, unless HMPA was the reaction solvent. In this case the crude reaction mixture was dissolved in CH_2Cl_2, and HMPA was extracted with water. The organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum. The *cis/trans* isomer distribution of the β-lactams was evaluated directly on the crude product material by ^1H NMR spectroscopy. The products were purified or separated by flash chromatography (SiO_2). Spectroscopic characteristics of azetidinones **2c**, *cis*- and *trans*-**2h**, and *cis*- and *trans*-**2i** have been reported.[5] Reaction conditions and yields are reported in Tables 1−3. For the MS, IR, ^1H NMR, and ^{13}C NMR spectral data and the microanalytical data of **2b**, **2d**, and **2g** see the supplementary material (Table 5). For the complete peak assignments of the ^1H NMR and ^{13}C NMR of β-lactams **2a**, **2e**, **2f**, **2l**, **2m**, **2n**, and **2o** see the supplementary material (Table 6).

(10) Santousso, T. M.; Swern, D. *Tetrahedron Lett.* **1968**, *40*, 4261.
(11) For an exhaustive account of the application of lanthanide reagents in organic synthesis, see: Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.
(12) Interestingly, a thermally-induced, 1,3-*H* shift has been observed in related four-membered ring heterocycles. For example, the isomerization of C3-monosubstituted 2-iminothietanes gives the corresponding thioacrylamides. See: Battaglia, A.; Giorgianni, P.; Dondoni, A. *J. Org. Chem.* **1980**, *45*, 3766.

Scheme 5



4-Phenyl-3,3-dimethyl-1-*p*-tolylazetidin-2-one (2a). Oxetane **1a** (0.32 g, 1.21 mmol) in the presence of Yb(HFC)$_3$ (0.03 g, 0.03 mmol) was allowed to react at 160 °C for 30 min; 0.25 g (0.94 mmol, 78%) of **2a** was obtained: mp 127−129 °C (C_6H_6/*n*-pentane); ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3H), 1.50 (s, 3 H), 2.26 (s, 3 H), 4.77 (s, 1 H), 6.93−7.47 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 18.0, 20.9, 22.9, 55.4, 66.5, 117.2, 126.6, 128.0, 128.7, 129.5, 133.2, 135.5, 135.8, 171.2; IR (CCl_4) 1767; mass spectrum *m/z* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47, H, 7.22; N, 5.28. Found: C, 81.38, H, 7.30; N, 5.19.

***cis*- and *trans*-4-Phenyl-3-methyl-3-vinyl-1-*p*-tolylazetidin-2-one (*cis*- and *trans*-2e).** (A) Oxetane *cis*-**1e** (0.24 g, 0.87 mmol) in the presence of Yb(FOD)$_3$ (0.02 g, 0.02 mmol) was allowed to react at 150 °C for 25 min. Chromatography of the reaction mixture (SiO_2, C_6H_6/Et_2O, 13:2) gave 0.05 g (0.17 mmol, 20%) of *trans*-**2e** and 0.07 g (0.27 mmol, 30%) of *cis*-**2e**. (B) Oxetane *trans*-**1e** (0.20 g, 0.72 mmol) in the presence of Yb(FOD)$_3$ (0.02 g, 0.02 mmol) was allowed to react at 150 °C for 25 min; 0.07 g (0.24 mmol, 33%) of *trans*-**2e** and 0.05 g (0.16 mmol, 23%) of *cis*-**2e** were obtained. *trans*-**2e**: mp 83−86 °C (Et_2O/*n*-pentane); ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 2.27 (s, 3 H), 4.97 (s, 1 H), 5.20−5.53 (m, 2 H), 6.00−6.33 (m, 1 H), 7.00−7.47 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.6, 20.9, 61.5, 65.5, 116.0, 117.3, 126.8, 128.1, 128.7, 129.6, 133.5, 135.0, 135.3, 137.8, 168.3; IR (CCl_4) 1767; mass spectrum *m/z* 277 (M^+), 199, 144. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.15, H, 6.98; N, 5.09. *cis*-**2e**: mp 95−97 °C (Et_2O/*n*-pentane); ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3 H), 2.25 (s, 3 H), 4.83 (s, 1 H), 4.90−5.10 (m, 1 H), 5.27−5.40 (m, 2 H), 6.90−7.43 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.8, 61.7, 67.2, 117.2, 117.3, 127.0, 128.2, 128.7, 129.5, 133.5, 134.4, 135.3, 135.4, 166.5; IR (CCl_4) 1765; mass spectrum *m/z* 277 (M^+), 199, 144; Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.15, H, 6.98; N, 5.09.

3-Methyl-1-(4-methoxyphenyl)azetidin-2-one (2f). Oxetane **1f** (0.25 g, 1.31 mmol) was allowed to react in the presence of Eu(HFC)$_3$ (0.03 g, 0.03 mmol) at 130 °C for 30 min; 0.16 g (0.85 mmol, 65%) of **2f** was obtained: mp 105−106 °C (C_6H_6/*n*-pentane); ^{1}H NMR ($CDCl_3$) δ 1.38 (d, 3 H), 3.19 (m, 1 H), 3.31 (m, 1 H), 3.72 (m, 1 H), 3.76 (s, 3 H), 6.80−7.30 (m, 4 H arom); J_{trans} = 2.5 Hz, J_{cis} = 5.5 Hz, J_{gem} = 5.5 Hz; ^{13}C NMR ($CDCl_3$) δ 13.7, 43.6, 46.2, 55.5, 114.4, 117.4, 132.3, 155.9, 167.6; IR (CCl_4) 1755; mass spectrum *m/z* 191 (M^+), 149, 135. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09, H, 6.85; N, 7.33. Found: C, 6.15, H, 6.80; N, 7.39.

***cis*- and *trans*-4-Prop-1-ynyl-3-methyl-1-(4-methoxyphenyl)azetidin-2-one (*cis*- and *trans*-2i).** (A) Oxetane *cis*-**1i** (0.23 g, 0.98 mmol) in the presence of Yb(FOD)$_3$ (0.05 g, 0.05 mmol) was allowed to react at 100 °C for 10 h. Chromatography of the reaction mixture (SiO_2, *n*-pentane/EtOAc, 13:4) gave 0.08 g (0.37 mmol, 38%) of *cis*-**2i** and 0.01g (0.04 mmol, 4%) of *trans*-**2l**. (B) Oxetane *cis*-**1i** (0.08 g, 0.34 mmol) dissolved in 1.5 mL of HMPA was allowed to react in the presence of Yb(FOD)$_3$ (0.01 g, 0.01 mmol) at 75 °C for 200 min. Chromatography of the reaction mixture gave 0.02 g (0.10 mmol, 28%) of *cis*-**2i**. (C) Oxetane *trans*-**1i** (0.10 g, 0.43 mmol) dissolved in 1.5 mL of HMPA was allowed to react in the presence of Yb(FOD)$_3$ (0.02 g, 0.02 mmol) at 75 °C for 200 min. Chromatography of the reaction mixture gave 0.01 g (0.02 mmol, 5%) of *cis*-**2i** and 0.02 g (0.08 mmol, 19%) of *trans*-**2i**.

***cis*- and *trans*-1-*p*-Tolyl-3-methyl-4-oxoazetidine-2-carboxylic Acid Methyl Ester (*cis*- and *trans*-2l).** (A) Oxetane *trans*-**1l** (0.11 g, 0.47 mmol) dissolved in 0.75 mL of HMPA was allowed to react at 130 °C for 90 min. Chromatography of the reaction mixture (SiO_2, C_6H_6/CH_3OH, 15:3) gave 0.05 g (0.20 mmol, 42%) of *trans*-**2l**. (B) Oxetane *trans*-**1l** (0.11 g, 0.47 mmol) dissolved in 0.75 mL of HMPA was allowed to react in the presence of Eu(HFC)$_3$ (0.01 g, 0.01 mmol) at 130 °C for 25 min. Chromatography of the reaction mixture (SiO_2, C_6H_6/CH_3OH, 15:3) gave 0.07 g (0.29 mmol, 62%) of *trans*-**2l**. (C) Oxetane *cis*-**1l** (0.15 g, 0.65 mmol) dissolved in 1.0 mL of HMPA was allowed to react in the presence of Eu(HFC)$_3$ (0.02 g, 0.02 mmol) at 130 °C for 120 min. Chromatography of the reaction mixture gave 0.06 g (0.24 mmol, 37%) of *cis*-**2l** and 0.01 g (0.05 mmol, 8%) of *trans*-**2l**. *trans*-**2l**: oil; ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 3 H), 2.28 (s, 3 H), 3.28 (m, 1 H), 3.72 (s, 3 H), 4.00 (m, 1 H), 7.00−7.20 (m, 4 H); $J_{H3,H4}$ *(trans)* = 2.5 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 13.3, 20.9, 50.3, 52.7, 58.2, 116.3, 129.7, 134.0, 135.2, 166.3, 170.4; IR (CCl_4) 1730; mass spectrum *m/z* 233 (M^+). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.05, H, 6.46; N, 6.11. *cis*-**2l**: oil; ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3 H), 2.30 (s, 3 H), 3.59 (m, 1 H), 3.75 (s, 3 H), 4.50 (m, 1 H), 7.00−7.20 (m, 4 H); $J_{H3,H4}$ *(cis)* = 6.0 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 9.6, 20.9, 47.9, 52.4, 55.7, 116.5, 129.7, 134.0, 135.1, 166.2 (N-C=O), 169.3; IR (CCl_4) 1730; mass spectrum *m/z* 233 (M^+). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.87, H, 6.53; N, 5.93.

***cis*- and *trans*-4-Furan-2-yl-3-methyl-1-(4-methoxyphenyl)azetidin-2-one (*cis*- and *trans*-2m).** Methyl *N*-(*p*-methoxyphenyl)ketene imine (0.44 g, 2.73 mmol) and furan 2-carboxaldehyde (0.27 g, 2.81 mmol) were allowed to react at 25 °C in CCl_4 (5.0 mml) in the presence of Yb(FOD)$_3$ (0.04 g, 0.04 mmol). The ^{1}H NMR of the reaction mixture performed after *80%* conversion of the reagents (4 h) revealed the presence of a *trans/cis* = 1:1.5 mixture of 2-iminooxetanes **1m** (ca. 60%), together with minor amounts (<15%) of *cis*- and *trans*-**2m** and of *cis*- and *trans*-2-propenylfuran (<10%). The reaction mixture was left at 25 °C for 2 days. The IR spectrum of the reaction solution revealed the presence of *p*-methoxyphenyl isocyanate (ν_{NCO} = 2270 cm^{-1}), and the ^{1}H NMR revealed the presence of resonances for *cis*- and for *trans*-**2m** (*trans/cis* = 1.7:1) and for *cis*- and *trans*-2-propenylfuran (*trans/cis* = 1:1.8) with a **2m**/alkenes ratio of 1.7:1. After filtration of 0.25 g of a polymeric residue, the solvent, the *p*-methoxyphenyl isocyanate, and *cis*- and *trans*-2-propenylfuran were removed at 25 °C under high vacuum (0.01 Torr) and collected in a trap. The crude residue was chromatographed (*n*-pentane/EtOAc, 11:4) to give 0.21 g (0.82 mmol, 31%) of a mixture of *cis*- and *trans*-**2m**: IR (CCl_4) 1762; mass spectrum *m/z* 257 (M^+). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.93, H, 5.80; N, 5.50. The CCl_4 solution containing the *p*-methoxyphenyl isocyanate and the *cis*- and *trans*-2-propenylfuran was allowed to stand for a week at 25 °C in the presence of Yt(FOD)$_3$ (0.05 g, 0.05 mmol). No formation of the corresponding β-lactams *cis*- and *trans*-**2m** was detected. Relevant ^{1}H NMR resonances for ***trans*-2-[(4-methoxyphenyl)imino]-4-furan-2-yl-3-methyloxetane** (*trans*-**1m**) appeared at δ 1.52 (d, 3 H, Me), 3.60−3.80 (m, 1 H, CHMe), 5.13 (d, 1 H, CHO); $J_{H3,H4}$ *(trans)* = 4.8 Hz. Relevant ^{1}H NMR resonances of ***cis*-2-[(4-methoxyphenyl)-imino]-4-furan-2-yl-3-methyloxetane** (*cis*-**1m**) appeared at δ 1.24 (d, 3 H, Me), 3.90−4.10 (m, 1 H, CHMe), 5.61 (d, 1 H, CHO); $J_{H3,H4}$ *(cis)* = 7.0 Hz. Relevant ^{1}H NMR resonances of ***cis*-2-propenylfuran** appeared at δ 1.98 (dd, 3 H, Me), 5.65 (d of q, 1 H, CHMe); $J_{H,Me}$ = 5.2 Hz $J_{HC=C,Me}$ = 1.7 Hz; $J_{H,H}$ *(cis)* = 11.8 Hz. Relevant ^{1}H NMR resonances of ***trans*-2-propenylfuran** appeared at δ 1.86 (d, 3 H, Me), 6.19 (d of q, 1 H, CHMe); $J_{H,Me}$ = 5.0 Hz; $J_{H,H}$ *(trans)* = 15.5 Hz. *trans*-**2m**: relevant ^{1}H NMR ($CDCl_3$) resonances appeared at δ 1.45 (d, 3 H), 3.46 (m, 1 H), 3.73 (s, 3 H), 4.59 (d, 1 H); $J_{H3,H4}$ *(trans)* = 2.4 Hz, $J_{H3,Me}$ = 7.4 Hz; relevant ^{13}C NMR resonances appeared at ($CDCl_3$) δ 13.0, 52.8, 55.8, 167.4. *cis*-**2m**: relevant ^{1}H NMR ($CDCl_3$) resonances appeared at δ 1.10 (d, 3 H), 3.65

(m, 1 H), 3.74 (s, 3 H), 5.13 (d, 1 H); $J_{H3,H4}$ *(cis)* = 5.6 Hz, $J_{H3,Me}$ = 7.5 Hz. Relevant ^{13}C NMR ($CDCl_3$) resonances appeared at δ 9.5, 49.7, 51.8, 167.5.

***cis*- and *trans*-4-Thiophene-2-yl-3-methyl-1-(4-methoxyphenyl)azetidin-2-one (*cis*- and *trans*-2n).** Methyl *N*-(*p*-methoxyphenyl)ketene imine (0.35 g, 2.17 mmol) and thiophene-2-carboxaldehyde (0.24 g, 2.13 mmol) were allowed to react at 25 °C in CCl_4 (5.0 mml) in the presence of Yb(FOD)$_3$ (0.04 g, 0.04 mmol). ^1H NMR of the reaction mixture performed after 70% conversion of the reagents (7 h) revealed the presence of a *trans/cis* = 1:2 mixture of 2-iminooxetanes **1n** (ca. 55%), together with minor amounts (<10%) of *cis*- and *trans*-**2n** and *cis*- and *trans*-2-propenylthiophene (<10%). The reaction mixture was left at 25 °C for 2 days. The IR spectrum of the reaction solution revealed the presence of *p*-methoxyphenyl isocyanate (ν_{NCO} = 2270 cm^{-1}), and the ^1H NMR revealed the absence of the resonances for *cis*- and *trans*-**1n** and the presence of resonances for *cis*- and *trans*-**2n** (*trans/cis* = 2:1) and for *cis*- and *trans*-2-propenylthiophene (*trans/cis* = 1:1.3) with a **2n**/alkenes ratio of 1.3:1. After filtration of 0.16 g of a polymeric residue, the solvent, the *p*-methoxyphenyl isocyanate, and *cis*- and *trans*-2-propenylthiophene were removed at 25 °C under high vacuum (0.01 Torr) and collected in a trap. The crude residue was chromatographed (*n*-pentane/EtOAc, 11:4) to give 0.18 g (0.66 mmol, 31%) of a mixture of *cis*- and *trans*-**2n** (*trans/cis* = 2:1). Additional chromatography allowed the separation of a fraction containing pure *trans*-**2n**. Pure compound *cis*-**2n** was obtained after the recrystallization (Et_2O, −15 °C) of a fraction containing a 1:3 mixture of *trans/cis*-**2n**. The CCl_4 solution containing *p*-methoxyphenyl isocyanate and *cis*- and *trans*-2-propenylthiophene was allowed to stand for 1 week at 25 °C in the presence of Yb(FOD)$_3$ (0.05 g, 0.05 mmol). No formation of the corresponding β-lactams *cis*- and *trans*-**2n** was detected. Relevant ^1H NMR resonances of ***trans*-2-[(4-methoxyphenyl)imino]-4-thiophene-2-yl-3-methyloxetane** (*trans*-**1n**) appeared at δ 1.52 (d, 3 H, Me), 3.60−3.80 (m, 1 H, CHMe), 5.40 (d, 1 H, CHO); $J_{H3,H4}$ *(trans)* = 4.5 Hz. Relevant ^1H NMR resonances of ***cis*-2-[(4-methoxyphenyl)imino]-4-thiophene-2-yl-3-methyloxetane** (*cis*-**1n**) appeared at δ 1.12 (d, 3 H, Me), 3.90−4.10 (m, 1 H, CHMe), 5.91 (d, 1 H, CHO); $J_{H3,H4}$ *(cis)* = 6.7 Hz. Relevant ^1H NMR resonances of ***cis*-2-propenylthiophene** appeared at δ 1.97 (dd, 3 H, Me), 5.68 (dd, 1 H, CHMe); $J_{H,Me}$ = 7.3 Hz $J_{HC=C,Me}$ = 1.7 Hz; $J_{H,H}$ *(cis)* = 11.5 Hz. Relevant ^1H NMR resonances of ***trans*-2-propenylthiophene** appeared at δ 1.85 (d of q, 3 H, Me), 6.04 (d of q, 1 H, CHMe); $J_{H,Me}$ = 6.7 Hz $J_{HC=C,Me}$ = 1.7 Hz; $J_{H,H}$ *(trans)* = 15.6 Hz. *trans*-**2n**: oil; ^1H NMR ($CDCl_3$) δ 1.48 (d, 3 H), 3.29 (m, 1 H), 3.75 (s, 3 H), 4.83 (d, 1 H), 6.80−7.30 (m, 7 H); $J_{H3,H4}$ *(trans)* = 2.3 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 13.0, 55.4, 56.2, 58.6, 114.3, 118.4, 125.6, 127.1, 131.2, 142.0, 156.1, 167.4; IR (CCl_4) 1762; mass spectrum *m/z* 273 (M^+). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 66.00, H, 5.46; N, 5.04. *cis*-**2n**: mp 101−103 °C (Et_2O); ^1H NMR ($CDCl_3$) δ 1.06 (d, 3 H), 3.68 (m, 1 H), 3.76 (s, 3 H), 5.39 (d, 1 H), 6.80−7.30 (m, 7 H); $J_{H3,H4}$ *(cis)* = 5.6 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 9.5, 49.8, 54.7, 167.6; IR (CCl_4) 1762; mass spectrum *m/z* 273 (M^+). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.67, H, 5.58; N, 5.0.

***cis* and *trans*-4-(1-Methylpyrrol-2-yl)-3-methyl-1-(4-methoxyphenyl)azetidin-2-one (*cis*- and *trans*-2o).** Methyl *N*-(*p*-methoxyphenyl)ketene imine (0.45 g, 2.98 mmol) and 1-methylpyrrole-2-carboxaldehyde (0.33 g, 3.00 mmol) were allowed to react at 40 °C in CCl_4 (4.0 mL) in the presence of Yb(FOD)$_3$ (0.05 g, 0.05 mmol) for 6 days. The crude reaction mixture was chromatographed (*n*-pentane/EtOAc, 11:4) to give 0.18 g (0.68 mmol, 23%) of *trans*-**2o** and 0.08 g (0.30 mmol, 10%) of *cis*-**2o**. *trans*-**2o**: oil; ^1H NMR ($CDCl_3$) δ 1.46 (d, 3 H), 3.26 (m, 1 H), 3.60 (s, 3 H), 3.72 (s, 3 H), 4.64 (d, 1 H), 6.00−7.30 (m, 7 H); $J_{H3,H4}$*(trans)* = 2.5 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 13.2, 34.4, 53.2, 55.4, 56.7, 107.4, 109.2, 114.3, 118.4, 124.2, 127.9, 131.6, 156.1, 167.6; IR (CCl_4) 1765; mass spectrum *m/z* 270 (M^+). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.17, H, 6.78; N, 10.44. *cis*-**2o**: mp 103−105 °C (Et_2O); ^1H NMR ($CDCl_3$) δ 0.99 (d, 3 H), 3.55−3.70 (m, 1 H), 3.60 (s, 3 H), 3.72 (s, 3 H), 5.18 (d, 1 H), 5.90−7.30 (m, 7 H); $J_{H3,H4}$*(cis)* = 5.4 Hz, $J_{H3,Me}$ = 7.5 Hz; ^{13}C NMR ($CDCl_3$) δ 9.5, 34.0, 49.4, 52.5, 55.4, 107.2, 109.4, 114.2, 118.6, 123.3, 126.0, 131.3, 155.9, 167.5; IR (CCl_4) 1765; mass spectrum *m/z* 270 (M^+). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.22, H, 6.65; N, 10.41.

Thermal Stability of β-Lactams 2d, 2e, 2f, 2g, and 2h. (A) β-Lactam **2d** (0.20 g, 0.75 mmol) in the presence of Yb(HFC)$_3$ (0.02 g, 0.02 mmol) was allowed to react at 125 °C for 25 min. Chromatography of the reaction mixture (SiO_2, *n*-pentane/EtOAc, 13:4) gave 0.12 g (0.44 mmol, 58%) of **2d**. (B) A 1:1 mixture of β-lactams **2e** (0.14 g, 0.51 mmol) in the presence of Yb(FOD)$_3$ (0.01 g, 0.01 mmol) was allowed to react at 150 °C for 25 min. Chromatography of the reaction mixture (SiO_2, C_6H_6/Et_2O, 13:2) gave 0.13 g (0.47 mmol, 92%) of a 1:1 *cis/trans* mixture of β-lactams **2e**. (C) β-Lactam **2f** (0.16 g, 0.85 mmol) in the presence of Eu(HFC)$_3$ (0.03 g, 0.03 mmol) was allowed to react at 130 °C for 30 min. Chromatography of the reaction mixture (SiO_2, C_6H_6/Et_2O, 13:2) gave 0.15 g (0.80 mmol, 94%) of **2f**. (D) A 1:1 *cis/trans* mixture of β-lactams **2g** (0.22 g, 1.01 mmol) in the presence of Yb(HFC)$_3$ (0.04 g, 0.04 mmol) was allowed to react at 200 °C for 120 min. Chromatography of the reaction mixture (SiO_2, *n*-pentane/EtOAc, 12:4) gave 0.18 g (0.82 mmol, 82%) of a 1:1 *cis/trans* mixture of β-lactams **2g**. (E) A 1:1 *cis/trans* mixture of β-lactams **2h** (0.20 g, 0.86 mmol) in the presence of Eu(HFC)$_3$ (0.04 g, 0.04 mmol) was allowed to react at 200 °C for 90 min. Chromatography of the reaction mixture (SiO_2, *n*-pentane/EtOAc, 12:4) gave 0.18 g (0.77 mmol, 90%) of a 1:1 *cis/trans* mixture of β-lactams **2h**.

General Procedure for the Synthesis of β-Keto Amides in DMSO solutions. The 2-iminooxetanes and DMSO were introduced into a vial under argon. The vial was sealed and thermostated at the selected temperature for the time required. The solvent was removed under vacuum (10^{-2} Torr). The products were purified by flash chromatography (SiO_2). Reaction conditions and yields are given in Table 4. For the microanalytical, MS, IR, ^1H NMR, and ^{13}C NMR spectral data of **3b**, **3g**, **3h**, **3p**, **3q**, and **3r** see the supplementary material (Table 7). For the complete peak assignments of the ^1H NMR and ^{13}C NMR of **3a** and **3e** see the supplementary material (Table 8).

2,2-Dimethyl-3-oxo-3-phenyl-*N*-*p*-tolylpropionamide (3a). Oxetane **1a** (0.80 g, 3.02 mmol) was allowed to react in DMSO (6.0 mL) at 140 °C for 5 h; 0.72 g (2.56 mmol, 85%) of **3a** was obtained: mp 120−122 °C (C_6H_6/*n*-pentane); ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 2.27 (s, 3 H), 6.97−8.03 (m, 9 H), 7.62−7.8 (b, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 24.2, 55.3, 120.3, 128.2, 128.6, 129.3, 132.6, 134.0, 134.9, 135.2, 171.4, 201.3; IR (CCl_4) 3412, 3400−3280, 1705, 1680; mass spectrum *m/e* 281 (M^+). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.77, H, 6.77; N, 4.93.

2,2-Dimethyl-3-oxopent-4-enoic Acid *p*-Tolylamide (3e). A *trans/cis*-mixture of oxetanes **1e** (0.41 g, 1.48 mmol; *trans/cis*=0.22) was allowed to react in DMSO (5.0 ml) at 150 °C for 30 min; 0.33 g (1.12 mmol, 76%) of **3e** was obtained: mp 136−138 °C (ethyl ether/*n*-hexane); ^1H NMR ($CDCl_3$) δ 1.77 (s, 3 H), 2.30 (s, 3 H), 5.18−5.43 (m, 2 H), 6.77 (m, 1 H), 7.00−7.53 (m, 8 H), 7.80−8.00 (m, 2 H); J_{trans} = 17.7 Hz, J_{cis} = 10.9 Hz; ^{13}C NMR ($CDCl_3$) δ 20.8, 22.7, 61.9, 118.0, 120.2, 128.5, 129.3, 129.5, 132.9, 134.6, 134.8, 135.8, 137.8, 169.6, 198.0; IR (CCl_4) 3440−3250, 1705, 1680; mass spectrum *m/e* 293 (M^+), 159. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.19; H, 6.48; N, 4.81.

Supplementary Material Available: Tables 5−8. Table 5: microanalytical, MS, IR, ^1H NMR, and ^{13}C NMR spectral data of β-lactams **2b**, **2d**, and **2g**. Table 6: complete peak assignments of the ^1H NMR and ^{13}C NMR of β-lactams **2a**, **2e**, **2f**, and **2l**−**o**. Table 7: microanalytical, MS, IR, ^1H NMR, and ^{13}C NMR spectral data of β-ketoamides **3b**, **3g**, **3h**, and **3p**−**r**. Table 8: complete peak assignments of ^1H NMR and ^{13}C NMR of β-ketoamides **3a** and **3e** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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