Articles

Stereoselective Synthesis of Vinyl Ethers by the Reaction of N-(Arylidene(or alkylidene)amino)-2-azetidinones with Ozone[†,1]

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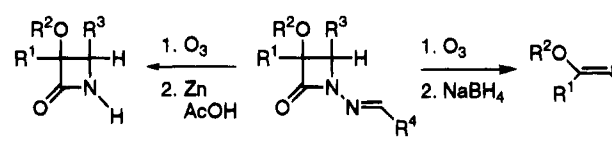
Ozonolysis of N-(arylidene(or alkylidene)amino)-2-azetidinones followed by $NaBH_4$ workup yields enol ethers in good yields with high levels of stereoselectivity. Di- and trisubstituted olefin derivatives are available through this procedure. Chiral 2-azetidinones lead to enol ethers with a chiral moiety without racemization. The reaction is thought to occur through a novel B-type fragmentation of the 2-azetidinone ring. This process is closely related to the well-known N-nitrosoamide to ester rearrangement and the decarboxylation of oxetan-2-ones.

Introduction

Widespread use of vinyl ethers and esters in organic synthesis[3] has promoted the development of an impressive variety of preparative methods to obtain these functional groups.[4] Main synthetic approaches to vinyl ethers include the alkylation of (α-methoxyvinyl)lithium,[5] carbometalation of alkynyl ethers by organocopper reagents,[6] Wittig−Horner reaction of α-alkoxy-substituted phosphorus ylides and related procedures,[7] Peterson olefin synthesis with [(trimethylsilyl)methoxy]methyl anions,[8] olefination of esters with Tebbe's and related reagents,[9] and O-alkylation of aldehydes and ketones under conditions directed to avoid the competitive C-alkylation.[10] Other less general methods have been reviewed.[4] Most of these synthetic methods yield Z/E mixtures of enol ethers, many being also nonregioselective. Therefore, searching for novel stereoselective entries to this interesting class of compounds is always desirable. Our recently reported synthesis of trisubstituted enol ethers by the reaction of alkoxychromium carbenes and sulfur ylides may be representative.[11] Included in a general project directed to develop different types of diazadienes as starting materials for β-lactam synthesis,[12] we have recently described a general synthesis of N-imino-β-lactams **1** and their use as substrates for the preparation of different non-β-lactam products.[13] One of the most striking characteristics of N-imino-β-lactams is their behavior toward ozone which can lead to vinyl ethers **2** through a novel fragmentation of the β-lactam ring or to NH-β-lactams **3** through N−N bond cleavage (Scheme 1).[13]

Scheme 1



3 **1** **2**

The sequential or simultaneous fragmentation of two bonds of the 2-azetidinone ring has been seldom reported. Cleavage of monocyclic β-lactams under electron-impact mass spectrometry occurs by two different fragmentation patterns, leading to ketene and/or imine ions (A-type) or to olefin and/or isocyanate ions (B-type) (Scheme 2).[14] Also, it is known that photolysis promotes cleavage of the 2-azetidinone ring[15] through an A-type fragmentation while pyrolysis[16] promotes the B-type fragmentation with complete retention of the stereochemistry of the starting 2-azetidinone, probably through a $[\sigma_{2s} - \sigma_{2a}]$ concerted mechanism. Formally, the formation of vinyl ethers from N-imino-β-lactams is a B-type fragmentation and is the

† Dedicated to the memory of Professor F. Serratosa.

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(1) For a preliminary communication of a part of this work, see: Alcaide, B.; Miranda, M.; Pérez-Castells, J.; Sierra, M. A. *J. Org. Chem.* **1993**, *58*, 297.

(2) Present address: Unidad de Química Orgánica, Universidad de San Pablo-CEU, Madrid.

(3) See, for example: Chan, T. H. in *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 2, pp 595−628.

(4) See ref 3, p 611.

(5) See, among others: (a) Baldwin, G. A.; Höfle, G. A.; Lever, O. W. *J. Am. Chem. Soc.* **1974**, *96*, 7125. (b) Russell, C. E.; Hegedus, L. S. *J. Am. Chem. Soc.* **1983**, *105*, 943.

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(12) (a) Alcaide, B.; Martín-Cantalejo, Y.; Plumet, J.; Rodríguez-López, J.; Sierra, M. A. *Tetrahedron Lett.* **1991**, *32*, 803. (b) Alcaide, B.; Martín-Cantalejo, Y.; Pérez-Castells, J.; Rodríguez-López, J.; Sierra, M. A. *J. Org. Chem.* **1992**, *57*, 5921.

(13) Alcaide, B.; Miranda, M.; Pérez-Castells, J.; Polanco, C.; Sierra, M. A. *J. Org. Chem.* **1994**, *59*, 8003.

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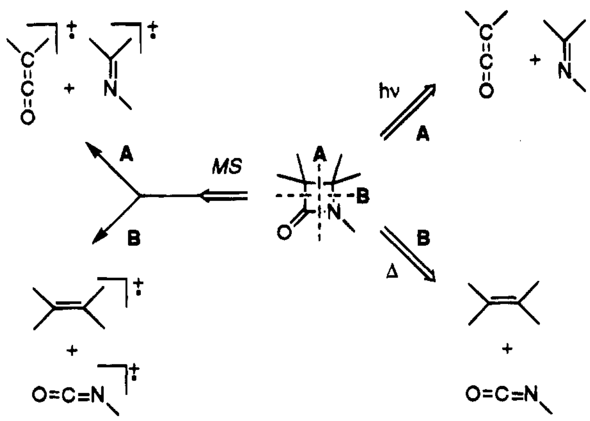
Scheme 2

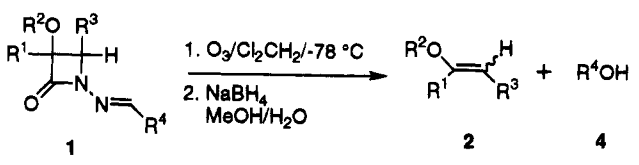


reverse of the well-known[17] olefin–isocyanate cycloaddition but with opposite regiochemistry. The scope and limitations of the formation of vinyl ethers from *N*-imino-β-lactams as well as data concerning the mechanism of this novel ring fragmentation are discussed here.

Results and Discussion

N-Imino-β-lactams **1** are easily available in multigram amounts from 2,3-diaza-1,3-dienes (azines) and different ketene precursors (free ketenes, acid chloride/Et_3N, and chromium(0) carbenes) according to our procedure.[13] The reaction of *N*-imino-β-lactams **1** with ozone at −78 °C followed by quenching with an excess of $NaBH_4$ (4 mol per mol of starting compound **1**) yields vinyl ethers **2** together with the corresponding primary alcohols **4** (Scheme 3). The cases studied are listed in Table 1. A variety of substituted enol ethers can be available through this methodology. Thus, disubstituted enol ethers having aliphatic (entries 1–8, 10–11, 13–14) as well as aromatic (entry 9) substituents at the oxygen are formed in moderate to good yields. Trisubstituted enol ethers (entries 15–18) and disubstituted enol ester (entry 12) are also produced efficiently. However, *N*-imino-β-lactams prepared from ketone-derived azines (acetophenone or cyclohexanone) and (benzyloxy)acetyl chloride reacted extremely slowly with ozone. In fact, traces of the corresponding olefins were detected by ^{1}H NMR after 48 h of ozonolysis. Although several ozonolysis conditions were tested, unreacted starting material was recovered in all cases.

Scheme 3



Chiral *N*-imino-β-lactams lead to the corresponding chiral enol ethers without racemization (entries 13 and 14). This last point deserves some additional comments. β-Lactam *cis*-**1k** is obtained in good yield by the reaction of optically pure (menthyloxy)acetyl chloride and the azine derived from anisaldehyde. Compound **1k** is formed as a mixture of both *cis*-diastereomers (3.8:1), enantiomers at the 2-azetidinone ring. However, the configuration of the two chiral centers of the 2-azetidinone ring is irrelevant to the final stereochemical outcome of the reaction, since both stereocenters are lost in the formation of the olefin. Therefore, the key point to obtaining chiral enol ethers is to control the *cis–trans* stereochemistry during the synthesis of the starting β-lactam. An analogous situation is the synthesis of chiral enol ethers from β-lactams having a chiral moiety attached at C4 (entry 14, Table 1).

Vinyl ethers are obtained with moderate to excellent *Z*/*E* selectivities. The stereochemistry of the major isomer reflects the starting 2-azetidinone (compare entries 1, 2, 7, 8, and 15–18), with levels of retention up to 100% (entry 11). The examples in Table 1 show that the bulkier the substituent at the C3 of the 2-azetidinone ring the better is the level of stereoselection. For example, the series of 2-azetidinones with Me, Bn, Ph, and *t*-Bu substituents at the C3 oxygen (entries 1 and 9–11) shows a steady increase in the *Z*/*E* selectivity from 72:28 to 100:0. This is not the case when substituents are attached to C4 of the 2-azetidinone ring (compare entries 3, 6, and 7, for example). The good selectivity obtained together with the possibility of preparing predominantly one of the two isomers across the double bond of the enol ether by selecting the adequate isomer of the starting 2-azetidinone make this process competitive with the previously reported synthetic methods for enol ethers.[3−10]

Some points must be considered prior to proposing a reaction pathway for this novel fragmentation of the 2-azetidinone ring. It is reasonable to assume that enol ethers are not the primary ozonolysis products but are formed upon $NaBH_4$ treatment. In fact, it is well known[18] that enol ethers are reactive toward ozone. Had these compounds been the primary reaction compounds they would have reacted with the excess of ozone to yield different reaction products. As depicted in Scheme 1, the nature of the reaction products clearly depends on the reaction workup. In fact, the use of Zn/AcOH instead of $NaBH_4$ to quench the mixtures of ozonization resulted in the exclusive formation of *NH*-β-lactams **3**.[13] Additionally, although the formation of enol ethers is highly selective, partial to moderate loss of the stereochemical integrity of the starting β-lactam is observed in most cases.[19] We can conclude that enol ethers and esters were not formed through a concerted pathway analogous to that proposed for the pyrolysis of 2-azetidinones which occurs with total retention of the configuration of the starting β-lactam.[16]

The reaction pathway which ultimately leads to compounds **2** should start with the electrophilic addition of ozone to the exocyclic imine double bond[20] followed by the usual evolution to ozonide **5** which may be the primary ozonolysis product. Decomposition of intermediate **5** by the action of $NaBH_4$ would result in the loss of the group attached to the exocyclic nitrogen as alcohol (which is the byproduct of these reactions) and rear-

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(19) The stereochemistry of enol ethers remains unaltered in the workup conditions. Thus, the pure, isolated mixture of enol ethers (*Z*/*E* 72:28) obtained from β-lactam *cis*-**1a** was submitted to $NaBH_4$ treatment under conditions identical to those used in the ozonolysis workup for 24 h. ^{1}H NMR analysis of the resulting mixture showed no changes in the isomer composition.

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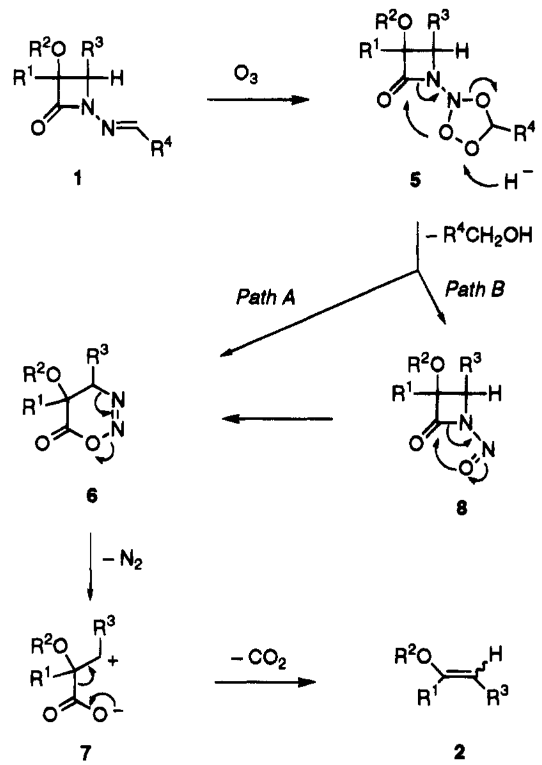
Table 1. Synthesis of Vinyl Ethers 2 from *N*-Imino-2-azetidinones 1

entry	substrate	R[1]	R[2]	R[3]	R[4]	product	*Z*/*E*[a]	yield[b] (%)
1	*cis*-**1a**	H	Bn	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2a**	72:28	64
2	*trans*-**1a**	H	Bn	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2a**	8:92	52
3	*cis*-**1b**	H	Bn	Ph	Ph	**2b**	95:5	77
4	*cis*-**1c**	H	Bn	*p*-MeC_6H_4	*p*-MeC_6H_4	**2c**	96:4	71
5	*cis*-**1d**	H	Bn	*m*-ClC_6H_4	*m*-ClC_6H_4	**2d**	93:7	50
6	*cis*-**1e**	H	Bn	*t*-Bu	*t*-Bu	**2e**	86:14	71
7	*cis*-**1f**	H	Bn	*i*-Pr	*i*-Pr	**2f**	77:23	44
8	*trans*-**1f**	H	Bn	*i*-Pr	*i*-Pr	**2f**	8:92	52
9	*cis*-**1g**	H	Ph	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2g**	91:9	75
10	*cis*-**1h**	H	Me	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2h**	72:28	60
11	*cis*-**1i**	H	*t*-Bu	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2i**	100:0	40
12	*trans*-**1j**	H	Ac	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2j**	33:67	78
13	*cis*-**1k**[c]	H	Ment[d]	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2k**	95:5	85
14	*cis*-**1l**	H	Bn	(*S*)-Ox[e]	*t*-Bu	**2l**	85:15	77
15	*cis*-**1m**	CH_3	Me	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2m**	86:14	75
16	*trans*-**1m**	CH_3	Me	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2m**	43:57	60
17	*cis*-**1n**	CH_3	Bn	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2n**	92:8	60
18	*trans*-**1n**	CH_3	Bn	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**2n**	12: 88	55

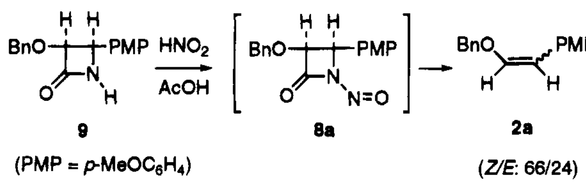
[a] Determined by integration of well-resolved signals in the ^1H NMR spectra of the crude mixtures prior to purification. [b] In pure isolated material (mixture of inseparable *E*/*Z* isomers) with correct analytical and spectral data. [c] A mixture of both *cis*-diastereomers was used. [d] Ment = (1*R*,2*S*,3*R*)-menthyl. [e] (*S*)-Ox = (*S*)-2,2-dimethyl-1,3-dioxolan-4-yl.

Scheme 4



rangement to the new intermediate **6** and hence to zwitterion **7** by loss of molecular nitrogen. Zwitterion **7** would form the final products by CO_2 elimination (path A, Scheme 4). In fact, the rearrangement of ozonide **5** to intermediate **6** is closely related to the well-known *N*-nitrosolactam to lactone rearrangement[21] while ylides **7** are thought to be intermediates in the synthetically useful decomposition of 2-oxetanones to form olefins.[22] Alternatively, ozonide **5** may evolve to *N*-nitroso-β-lactams **8** by the effect of $NaBH_4$. Intermediate **8** would later evolve to **6** by attack of the oxygen to the lactam carbonyl followed by cleavage of the amide bond of the former β-lactam ring (path B, Scheme 4).

Although preliminary results[1] obtained in the nitrosation of 4-*p*-anisyl-3-(benzyloxy)-2-azetidinone (**9**) (eq 1)



(1)

suggested that *N*-nitroso-β-lactams similar to **8a** may be the actual intermediates in enol ether formation, we were unable to obtain reproducible results in this and analogous reactions.[23] Therefore, distinction between both reaction pathways based on these results would be at least speculative.

In conclusion, an efficient and stereoselective synthesis of vinyl ethers and esters from readily available *N*-imino-β-lactams has been developed. The reaction occurs through a novel B-type fragmentation of the β-lactam ring under exceptionally mild reaction conditions.

Experimental Section

General Procedure. General experimental data and procedures have been previously reported.[24] All commercially available compounds were used without further purification. *N*-Imino-β-lactams **1** were prepared according to our reported[13] procedure and were used in all cases as single *cis*- or *trans*-isomers. Spectroscopic data (^1H and ^{13}C NMR) were obtained in $CDCl_3$ solutions in all cases.

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(23) The reaction of 2-azetidinone **9** in the conditions reported in eq 1 gave erratic results in the different experiments tested. Other reaction conditions such as *N*-nitrosation under neutral conditions (using CH_2Cl_2 or the mixture $CH_2Cl_2/EtOH/H_2O$ as solvents or other reagents ($NOBF_4$)) always led to unreacted material or very complex reaction mixtures. These results agree with those reported by Testa for nitrosation of C4-substituted *NH*-β-lactams which led to complex reaction mixtures while analogous reaction on C4-unsubstituted compounds produced *N*-nitroso-2-azetidinones. See: Pifferi, G.; Consonni, P.; Testa, E. *Gazz. Chim. Ital.* **1967**, *97*, 1719.

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***cis*-4-(*p*-Anisyl)-1-[(*p*-anisylmethylidene)amino]-3-[(1*R*,2*S*,5*R*)-menthyloxy]-2-azetidinone (1m).** A solution of [(1*R*,2*S*,5*R*)-menthyloxy]acetyl chloride (0.4 g, 2.2 mmol) in anhydrous toluene (5 mL) was added dropwise via syringe to a refluxing solution of *p*-anisaldehyde azine (0.536 g, 2.0 mmol) in toluene (10 mL) containing triethylamine (0.3 g, 3 mmol) under argon. The mixture was stirred for 2 h. Then, the reaction mixture was cooled, diluted with $CHCl_3$, successively washed with aqueous $NaHCO_3$ (saturated solution, 20 mL) and water (2 × 10 mL), and dried ($MgSO_4$). After filtration and evaporation of the solvent under reduced pressure, ^{1}H-NMR analysis showed a mixture of diastereomeric *cis*-*N*-imino-β-lactams **1m** (3.8:1). Flash chromatography of the mixture gave 0.835 g (90%) of the analytically pure mixture as a white solid. An analytically pure sample of the major isomer was obtained by crystallization (EtOH). **Major Isomer.** White crystalline solid. Mp: 141–143 °C (EtOH). $[\alpha]_D$ = +81.4 (c = 0.048 g/100 mL, EtOH). ^{1}H NMR: δ 0.26 (d, 3H, J = 6.9 Hz), 0.58 (d, 3H, J = 6.9 Hz), 0.74–0.79 (m, 2H), 0.89 (d, 3H, J = 6.6 Hz), 0.94–1.04 (m, 2H), 1.22–1.29 (m, 2H), 1.43–1.47 (m, 1H), 1.54 (m, 1H), 2.13–2.17 (m, 1H), 2.97 (td, 1H, J_1 = 4.5 Hz, J_2 = 10.8 Hz), 3.78 (s, 6H), 4.83 (d, 1H, J = 4.8 Hz), 5.20 (d, 1H, J = 4.8 Hz), 6.81 (d, 2H), 6.84 (d, 2H), 7.24 (d, 2H), 7.53 (m, 2H), 7.70 (s, 1H). ^{13}C NMR: δ 164.6, 161.7, 160.0, 146.0, 129.4, 129.3, 126.2, 124.8, 114.2, 114.1, 81.1, 80.2, 65.1, 55.4 (2C), 47.7, 41.0, 34.3, 31.6, 24.6, 23.0, 22.4, 20.9, 16.0. IR ($CHCl_3$): ν 1755, 1610, 1590, 1520, 1390, 1320 cm^{-1}. Anal. Calcd for $C_{28}H_{36}N_2O_4$: C, 72.37, H, 7.81; N, 6.03. Found: C, 72.46; H, 7.99; N, 5.93.

General Procedure for the Ozonolysis of *N*-Imino-2-azetidinones, 1. A stream of ozonized oxygen was bubbled through a solution of *N*-imino-β-lactam **1** (1 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After completion of the reaction (TLC), the excess ozone was removed by bubbling argon for 10 min. The resulting solution was then poured onto a solution of $NaBH_4$ (4 mmol) in EtOH/H_2O (1:1) at 0 °C. After vigorous stirring for 12 h at room temperature, the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL) and dried ($MgSO_4$). Evaporation of the solvents gave crude compounds **2** as an inseparable Z/E mixture which was chromatographed (silica gel, hexane/EtOAc mixtures) to afford an analytically pure mixture of both isomers.

In all cases the Z/E isomer ratio for compounds **2** was calculated by integration of the appropriate well-resolved signals of the crude reaction mixtures. Spectroscopic data are listed from spectra of pure Z/E mixtures, which were also used for analytical determinations. Assignment of Z/E stereochemistry was made on the basis of the coupling constants of the vinyl protons (for Z isomers J = 6.0–7.2 Hz and for E isomers J = 12.6–13.2 Hz), except for compounds **2m** and **2n**. The stereochemistry of compounds **2m** and **2n** was established by NOE measurements. Thus, irradiation of the methyl group of the *cis*-isomer resulted in an increment of the vinyl proton of 17% and 8%, respectively. An analogous experiment realized on the *trans* isomers showed no NOE increment. Except when otherwise stated data for the major isomer in the Z/E mixture are listed.

2-(*p*-Anisyl)-1-(benzyloxy)ethene (2a). From *cis*-1a (*Z*/*E* 72:28). From 0.416 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1a** was obtained 0.16 g (64%) of the analytically pure mixture as a colorless oil. Reaction time: 0.75 h. ^{1}H-NMR: δ 3.76 (s, 3H), 4.94 (s, 2H), 5.21 (d, 1H, J = 6.9 Hz), 6.17 (d, 1H, J = 6.9 Hz), 6.83 (d, 2H), 7.25–7.38 (m, 5H), 7.56 (d, 2H). ^{13}C-NMR: δ 157.6, 144.6, 137.3, 129.4 (2C), 128.7, 128.5, 127.2, 113.6, 105.8, 74.7, 55.1. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.71; H, 6.60. **From *trans*-1a (*Z*/*E* 8:92).** From 0.416 g (1.0 mmol) of *N*-imino-β-lactam *trans*-**1c** was obtained 0.125 g (52%) of the analytically pure mixture as a colorless oil. Reaction time: 0.75 h. ^{1}H-NMR: δ 3.74 (s, 3H), 4.83 (s, 2H), 5.88 (d, 1H, J = 13.0 Hz), 6.77 (d, 2H), 6.92 (d, 1H, J = 13.0 Hz), 7.11 (d, 2H), 7.17–7.95 (m, 5H). ^{13}C-NMR: δ 157.9, 146.3, 136.8, 129.5, 128.5, 128.0, 127.6, 126.2, 114.1, 106.4, 71.8, 55.3. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.12; H, 6.79.

1-(Benzyloxy)-2-phenylethene (2b) (*Z*/*E* 95:5). From 0.354 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1b** was obtained 0.161 g (77%) of the analytically pure mixture as a colorless oil. ^{1}H NMR: δ 4.96 (s, 2 H), 5.25 (d, 1H, J = 6.9 Hz), 6.26 (d, 1H, J = 6.9 Hz), 7.10–7.18 (m, 1H), 7.25–7.40 (m, 3H), 7.35–7.37 (m, 4H), 7.60–7.64 (m, 2H). ^{13}C NMR: δ 146.2, 137.2, 135.8, 128.5, 128.3, 128.2, 128.0, 127.2, 125.7, 106.2, 74.9. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.91; H, 6.78.

1-(Benzyloxy)-2-(*p*-tolyl)ethene (2c) (*Z*/*E* 96:4). From 0.334 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1c** was obtained 0.159 g (71%) of the analytically pure mixture as a colorless oil. Reaction time: 3 h. ^{1}H NMR: δ 2.28 (s, 3 H), 4.91 (s, 2 H), 5.21 (d, 1H, J = 7.2 Hz), 6.18 (d, 1H, J = 7.2 Hz), 7.06 (d, 2H), 7.32 (m, 5H), 7.50 (d, 2H). ^{13}C NMR: δ 145.4, 137.2, 135.2, 132.9, 128.7, 128.4, 128.1, 127.8, 127.0, 106.1, 74.6, 21.0. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 86.01; H, 7.26.

1-(Benzyloxy)-2-(*m*-chlorophenyl)ethene (2d) (*Z*/*E* 93:7). From 0.393 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1d** was obtained 0.113 g (50%) of the analytically pure mixture as a colorless oil. Reaction time: 9 h. ^{1}H NMR: δ 4.99 (s, 2H), 5.19 (d, 1H, J = 7.2 Hz), 6.29 (d, 1H, J = 7.2 Hz), 7.03–7.24 (m, 2H), 7.33–7.37 (m, 5H), 7.40–7.43 (m, 1H), 7.63–7.65 (m, 1H). ^{13}C NMR: δ 147.3, 137.6, 136.7, 134.0, 129.3, 128.6, 128.1, 128.0, 127.6, 126.3, 125.7, 121.7, 105.0, 75.1. Anal. Calcd for $C_{15}H_{13}OCl$: C, 73.62; H, 5.35; Cl, 14.49. Found: C, 73.92; H, 5.23; Cl, 14.56.

1-(Benzyloxy)-3,3-dimethyl-1-butene (2e) (*Z*/*E* 86:14). From 0.316 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1e** was obtained 0.152 g (71%) of the analytically pure mixture as a colorless oil. Reaction time: 4 h. ^{1}H NMR: δ 1.13 (s, 9H), 4.22 (d, 1H, J = 6.9 Hz), 4.68 (s, 2H), 5.82 (d, 1H, J = 6.9 Hz), 7.33 (m, 5H). ^{13}C NMR: δ 143.2, 137.3, 128.3, 127.5, 127.0, 117.2, 71.0, 30.8, 30.5. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.25; H, 9.60.

1-(Benzyloxy)-3-methyl-1-butene (2f). From *cis*-1f (*Z*/*E* 77:23). From 0.288 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1f** was obtained 0.08 g (44%) of the analytically pure mixture as a colorless oil (bp = 90 °C) by distillation of the crude mixture. Reaction time: 0.75 h. ^{1}H-NMR: δ 0.94 (d, 6H, J = 9.0 Hz), 2.80 (m, 1H), 4.25 (dd, 1H, J_1 = 6.0 Hz, J_2 = 9.0 Hz), 4.76 (s, 2H), 5.88 (dd, 1H, J_1 = 6.0 Hz, J_2 = 0.9 Hz), 7.30–7.34 (m, 5H). ^{13}C-NMR: δ 142.7, 136.7, 128.4, 127.7, 127.2, 115.7, 73.5, 23.9, 23.2. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.59; H, 9.01. **From *trans*-1f (*Z*/*E* 8:92).** From 0.288 g (1.0 mmol) of *N*-imino-β-lactam *trans*-**1f** was obtained 0.09 g (52%) of the analytically pure mixture as a colorless oil (bp = 85 °C) by distillation of the crude mixture. ^{1}H-NMR: δ 0.98 (d, 6H, J = 7.2 Hz), 2.28 (m, 1H), 4.67 (s, 2H), 4.85 (dd, 1H, J_1 = 7.2 Hz, J_2 = 12.6 Hz), 6.32 (d, 1H, J = 12.6 Hz), 7.32 (m, 5H). ^{13}C-NMR: δ 144.2, 137.3, 128.4, 127.7, 127.5, 112.7, 71.0, 27.5, 23.7. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.11.

2-(*p*-Anisyl)-1-phenoxyethene (2g) (*Z*/*E* 91:9). From 0.4 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1g** was obtained 0.17 g (75%) of the analytically pure mixture as a colorless oil. Reaction time: 1 h. ^{1}H NMR: δ 3.79 (s, 3 H), 5.57 (d, 1H, J = 6.9 Hz), 6.52 (d, 1H, J = 6.9 Hz), 6.85 (d, 2H), 7.08–7.17 (m, 2H), 7.24 (s, 1H), 7.31–7.35 (m, 2H), 7.61 (d, 2H). ^{13}C NMR: δ 158.4, 157.4, 140.2, 130.1, 129.8, 127.8, 123.3, 116.9, 113.9, 110.3, 55.4. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.89; H, 6.30.

2-(*p*-Anisyl)-1-methoxyethene (2h) (*Z*/*E* 72:28). From 0.293 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1i** was obtained 0.1 g (60%) of the analytically pure mixture as a colorless oil. ^{1}H-NMR: δ 3.75 (s, 3H), 3.79 (s, 3H), 5.17 (d, 1H, J = 6.9 Hz), 6.05 (d, 1H, J = 6.9 Hz), 6.83 (d, 2H), 7.52 (d, 2H). ^{13}C-NMR: δ 157.5, 146.3, 130.2, 129.3, 113.5, 105.1, 60.4, 55.1. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.22; H, 7.41.

2-(*p*-Anisyl)-1-*tert*-butoxyethene (2i) (*Z*/*E* 100:0). From 0.382 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1i** was obtained 0.085 g (40%) of analytically pure compound **2i** as a colorless oil. Reaction time: 1.5 h. ^{1}H NMR: δ 1.37 (s, 9H), 3.78 (s, 3H), 5.20 (d, 1H, J = 7.2 Hz), 6.60 (d, 1H, J = 7.2 Hz), 6.83 (d, 2H), 7.57 (d, 2H). ^{13}C NMR: δ 157.2, 139.2, 129.4, 129.2, 113.5, 105.2, 55.1, 41.7, 28.0. IR ($CHCl_3$): ν 1650, 1610, 1580, 1510, 1470, 1430 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.45; H, 8.90.

1-Acetoxy-2-(*p*-anisyl)ethene (2j) (*Z*/*E* 33:67). From 0.368 g (1.0 mmol) of *N*-imino-β-lactam *trans*-**1j** was obtained 0.15 g (78%) of the analytically pure mixture as a colorless oil. Reaction time: 2 h. **(*E*)-Isomer.** ^{1}H NMR: δ 2.17 (s, 3H), 3.79 (s, 3H), 6.34 (d, 1H, J = 12.6 Hz), 6.83 (d, 2H), 7.25 (d, 2H), 7.73 (d, 1H, J = 12.6 Hz). ^{13}C NMR: δ 168.1, 159.1, 134.8, 130.4, 127.4, 114.1, 113.8, 55.3, 29.7. **(*Z*)-Isomer.** ^{1}H NMR: δ 2.25 (s, 3H), 3.81 (s, 3H), 5.64 (d, 1H, J = 7.2 Hz), 6.87 (d, 2H), 7.20 (d, 1H, J = 7.2 Hz), 7.52 (d, 2H). ^{13}C NMR: δ 163.9, 159.3, 134.8, 132.4, 126.5, 114.8, 111.3, 52.3, 29.3. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.81; H, 6.23.

2-(*p*-Anisyl)-1-[(1*R*,2*S*,5*R*)-menthyloxy]ethene (2k) (*Z*/*E* 95:5). From 0.4 g (1.0 mmol) of the mixture of *cis*-stereoisomers of *N*-imino-β-lactam *cis*-**1k** was obtained 0.245 g (85%) of the analytically pure mixture as a colorless oil. Reaction time: 0.75 h. ^{1}H NMR: δ 0.78 (d, 3H, J = 6.9 Hz), 0.91 (d, 6H, J = 6.9 Hz), 0.87−0.92 (m, 1H), 0.94−1.16 (m, 2H), 1.24−1.57 (m, 2H), 1.60−1.69 (m, 2H), 2.01−2.10 (m, 1H), 2.20 (dt, 1H, J = 7.2, 3.0 Hz), 3.50 (td, 1H, J_1 = 10.5 Hz, J_2 = 4.5 Hz), 3.78 (s, 3H), 5.11 (d, 1H, J = 6.9 Hz), 6.16 (d, 1H, J = 6.9 Hz), 6.81 (d, 2H), 7.52 (d, 2H). ^{13}C NMR: δ 157.3, 144.7, 129.4, 129.1, 113.6, 104.3, 83.4, 55.2, 47.9, 41.9, 34.3, 31.6, 25.9, 23.4, 22.2, 16.4, 16.0. Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.45; H, 9.80.

1-(Benzyloxy)-2-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]ethene (2l) (*Z*/*E* 85:15). From 0.36 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1l** was obtained 0.18 g (77%) of the analytically pure mixture as a colorless oil. Reaction time: 1.5 h. ^{1}H NMR: δ 1.37 (s, 3H,), 1.39 (s, 3H), 3.48 (t, 1H, J = 8.1 Hz), 4.07 (dd, 1H, J = 8.1 Hz, J = 6.3 Hz), 4.49 (dd, 1H, J = 8.4, 6.3 Hz), 4.80 (AB, 2H, J = 12.6 Hz), 5.07 (dd, 1H, J_1 = 6.3 Hz, J_2 = 1.2 Hz), 6.19 (dd, 1H, J_1 = 6.3 Hz, J_2 = 1.2 Hz), 7.21−7.33 (m, 5H). ^{13}C NMR: δ 148.1, 136.9, 128.5, 128.1, 127.4, 108.6, 104.8, 74.2, 70.1, 69.5, 26.8, 25.9. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.54; H, 7.70.

1-(*p*-Anisyl)-2-methoxypropene (2m). From *cis*-1m (*Z*/*E* 86:14). From 0.382 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1m** was obtained 0.084 g (75%) of the analytically pure mixture as a colorless oil. Reaction time: 2 h. ^{1}H NMR: δ 2.10 (s, 3H), 3.66 (s, 3H), 3.77 (s, 3H), 5.25 (s, 1H), 6.86 (d, 2H), 7.26 (d, 2H). ^{13}C NMR: δ 157.2, 140.8, 129.8, 129.0, 113.4, 98.7, 55.2, 54.4, 18.4. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.48; H, 7.80. **From *trans*-1m (*Z*/*E* 43:57).** From 0.382 g (1.0 mmol) of *N*-imino-β-lactam *trans*-**1m** was obtained 0.067 g (60%) of the analytically pure mixture as a colorless oil. Reaction time: 2.75 h. ^{1}H NMR: δ 1.95 (s, 3H), 3.62 (s, 3H), 3.78 (s, 3H), 5.52 (s, 1H), 6.83 (d, 2H), 7.09 (d, 2H). ^{13}C NMR: δ 155.4, 140.8, 130.2, 129.7, 113.6, 99.7, 55.2, 54.5, 17.7. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.44; H, 7.82.

2-(*p*-Anisyl)-1-(benzyloxy)propene (2n). From *cis*-1n (*Z*/*E* 92:8). From 0.43 g (1.0 mmol) of *N*-imino-β-lactam *cis*-**1n** was obtained 0.153 g (60%) of the analytically pure mixture as a white solid. Reaction time: 2 h. ^{1}H NMR: δ 2.01 (s, 3H), 3.77 (s, 3H), 4.83 (s, 2H), 5.64 (s, 1H), 6.82 (d, 2H), 7.09 (d, 2H), 7.20−7.40 (m, 5H). ^{13}C NMR: δ 157.3, 154.7, 137.2, 130.1, 129.7, 128.5, 127.8, 127.6 113.6, 100.1, 69.1, 55.2, 17.9. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.56; H, 7.02. **From *trans*-1n (*Z*/*E* 12:88).** From 0.43 g (1.0 mmol) of *N*-imino-β-lactam *trans*-**1n** was obtained 0.14 g (55%) of the analytically pure mixture as a colorless oil. Reaction time: 2 h. ^{1}H NMR: δ 2.03 (s, 3H), 3.78 (s, 3H), 4.96 (s, 2H), 5.31 (s, 1H), 6.78 (d, 2H), 7.21−7.30 (m, 2H), 7.33−7.36 (m, 3H), 7.57 (d, 2H). ^{13}C NMR: δ 154.3, 144.7, 131.2, 128.4, 128.3, 128.2, 127.3, 127.2, 113.3, 102.6, 62.9, 55.2, 22.1. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.63; H, 6.94.

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