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Cyclizative radical carbonylations of azaenynes by TTMSS and hexanethiol leading to α-silyl- and thiomethylene lactams. Insights into the *E*/*Z* stereoselectivities† ‡

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Free-radical mediated cyclizative carbonylations of azaenynes were carried out using TTMSS as a radical mediator to compare the efficiency and the stereochemistry with those using tributyltin hydride. Using a substrate concentration of 0.1 M, the reactions gave good yields of α-silylmethylene lactams having four to seven-membered rings. The observed *E*-diastereoselectivity of the resulting vinylsilane moiety is in sharp contrast to the *Z*-selectivity observed during the analogous carbonylation using tributyltin hydride. When hexanethiol was used as the radical mediator, α-thiomethylene lactams were formed with *E*-favoring stereoselectivity again. *Ab initio* and DFT molecular orbital calculations on the stability of *E* and *Z* products were carried out for a set of five-membered methylene lactams bearing SnH_3, SiH_3, and SMe groups. The distinct thermodynamic preference for the *Z*-isomer was only predicted for the Sn-bearing lactam. A steric effect due to the bulky $(TMS)_3Si$ group is proposed for the *E*-selectivity observed in the TTMSS-mediated reaction.

Introduction

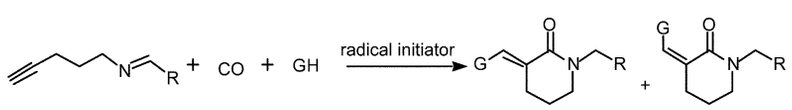
The creation of efficient and selective cyclization methods to construct carbocyclic and heterocyclic rings is one of the main goals in modern radical chemistry.[1,2] We are interested in developing powerful radical annulation strategies which incorporate carbon monoxide into rings.[3,4] Inspired by initial efforts in this area, in paricular in the exploration of alkyl, vinyl, and aryl radical cyclizations onto N–C double bonds,[5,6] we recently chose to examine in detail $n + 1$ annulation strategies directed toward the synthesis of nitrogen-containing heterocycles. Radical carbonylation chemistry with the subsequent acyl radical cyclization onto N–C double bonds proved to be effective in this area. In particular we found that acyl radical cyclization onto imine N–C bonds is a highly efficient process that proceeds in complete *N*-philic mode to give good yields of 2-pyrrolidinones.[7] *Ab initio* and density functional (DFT) molecular orbital calculations predict that the transition state involved in the cyclization onto the N–C double bond is highly influenced by polar factors.[8]

Recently we also found that stannylcarbonylation of azaenynes using tributyltin hydride and carbon monoxide provides a useful method for the synthesis of α-stannylmethylene lactams.[9] This tin-mediated *N*-philic cyclization permits a wide scope of cyclization modes covering 4-*exo*, 5-*exo*, 6-*exo*, 7-*exo*, and 8-*exo*. As for the stereoselectivity of these reactions with respect to the resulting vinyltin unit, generally *Z*-isomeric alkenes were obtained as the major products, as exemplified by the first example in Scheme 1.

The aim of this work is to expand the carbonylation cyclization strategy to include some other useful free-radical chain processes, such as tris(trimethylsilyl)silane (TTMSS)[10] or hexanethiol mediated processes, which should give rise to the related lactams that are substituted with a [tris(trimethylsilyl)]silyl or a hexylthio functionality at the vinylic moiety in these products. In these two variants, *E*-stereoselectivity was generally observed, which is in contrast to the *Z*-selectivity observed for the corresponding tributyltin hydride mediated reaction (Scheme 1). These differing stereochemical outcomes will be discussed together with the results of *ab initio* and DFT molecular orbital calculations which shed light on some of the factors that influence the stability of the various *E* and *Z* products in this study.

† Electronic supplementary information (ESI) available: spectroscopic data for **2a**–**2d**, **2f**, and **3a**–**3d**, **3f** and optimized geometries and energies for all model compounds in this study (Gaussian Archieve entries). See http://www.rsc.org/suppdata/ob/b3/b309944j/

‡ Dedicated to Professor Noboru Sonoda on the occasion of his 70th birthday.



1e R = *i*-Pr

GH = Bu_3SnH (reference 9)	E/Z = 0/100
GH = $(TMS)_3SiH$ (this work)	E/Z = 100/0
GH = $C_6H_{13}SH$ (this work)	E/Z = 100/0

Scheme 1 *E*/*Z* Selectivities in cyclizative radical carbonylations of azaenyne **1e**.

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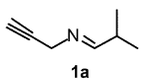
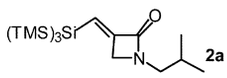
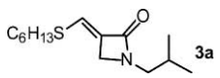
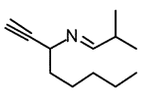
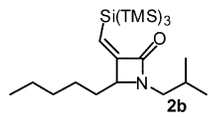
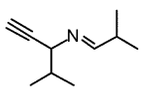
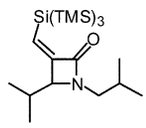
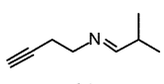
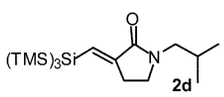
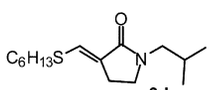
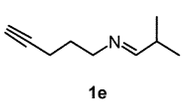
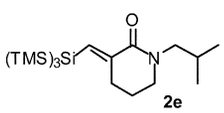
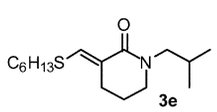
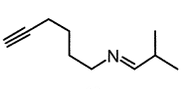
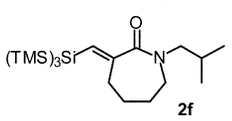
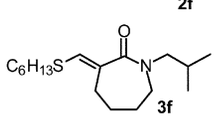
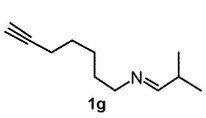
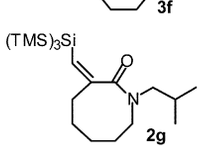
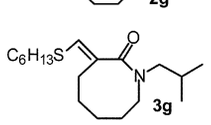
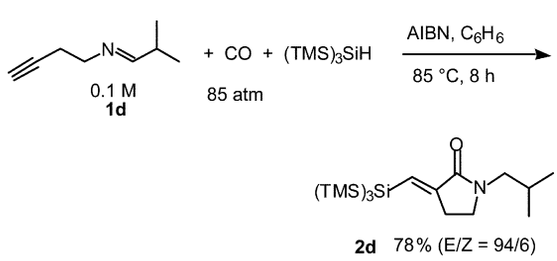
Table 1 Silyl- and thiocarbonylation of azaenynes **1** leading to lactams **2** and **3**[a]

Run	Azaenyne **1**	Conditions	Lactams **2** and **3**	Yield[b] (*E* : *Z*)[c]
1	 **1a**	TTMSS 0.1 M, CO 87 atm, 85 °C, 8 h	 **2a**	71% (85 : 15)
2	**1a**	$C_6H_{13}SH$ 0.01 M, CO 85 atm, 110 °C, 12 h	 **3a**	45% (86 : 14)
3	 **1b**	TTMSS 0.1 M, CO 88 atm, 85 °C, 8 h	 **2b**	67% (27 : 63)
4	 **1c**	TTMSS 0.1 M, CO 88 atm, 85 °C, 8 h	 **2c**	34% (14 : 86)
5	 **1d**	TTMSS 0.1 M, CO 85 atm, 85 °C, 8 h	 **2d**	78% (94 : 6)
6	**1d**	$C_6H_{13}SH$ 0.01 M, CO 85 atm, 110 °C, 12 h	 **3d**	45% (100 : 0)
7	 **1e**	TTMSS 0.1 M, CO 85 atm, 85 °C, 8 h	 **2e**	72% (100 : 0)
8	**1e**	$C_6H_{13}SH$ 0.01 M, CO 85 atm, 110 °C, 12 h	 **3e**	60% (100 : 0)
9	 **1f**	TTMSS 0.1 M, CO 85 atm, 85 °C, 8 h	 **2f**	54% (85 : 15)
10	**1f**	$C_6H_{13}SH$ 0.01 M, CO 85 atm, 110 °C, 12 h	 **3f**	55% (85 : 15)
11	 **1g**	TTMSS 0.1 M, CO 85 atm, 85 °C, 8 h	 **2g**	20% (38 : 62)
12	**1g**	$C_6H_{13}SH$, 0.01 M, CO 85 atm, 110 °C, 12 h	 **3g**	20% (31 : 69)

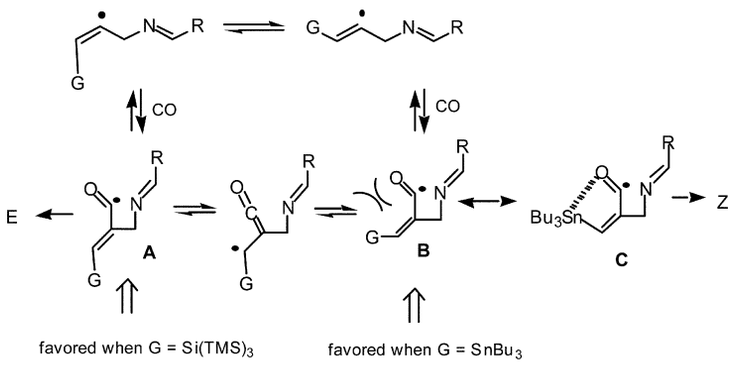
[a] Conditions: silylcarbonylation; **1** (1 mmol), TTMSS (1.1–1.4 mmol), AIBN (20–30 mol%), benzene (10 ml), CO (85–88 atm). Thiocarbonylation; **1** (0.5 mmol), $C_6H_{13}SH$ (1.1–1.4 mmol), V-40 (40 mol%), benzene (50 ml), CO (90 atm). For typical procedure, see Experimental section. [b] Isolated yields by flash chromatography on silica gel. [c] Determined by ^1H NMR of crude reaction mixture.

Results and discussion

TTMSS delivers hydrogen to a carbon radical center at a slower rate than tributyltin hydride.[11] Thus, we expected that the carbonylation reaction with TTMSS[12] could be carried out even under concentrated conditions without suffering from the premature quenching of the vinyl radical species involved in this reaction by TTMSS, leading to unwanted uncyclized vinylsilanes. After surveying the reaction conditions using azaenyne **1d** as a model substrate, we found that rather high substrate concentrations, such as 0.1 M, are suitable for efficient chain propagation. For example, when a benzene solution containing **1d**, 1.1 equiv. of TTMSS, and 20 mol% of AIBN (2,2′-azobisisobutyronitrile) was treated with 85 atm of carbon monoxide at 85 °C for 8 h, 5-silylmethylene-2-azacyclopentanone **2d** was obtained in 78% yield after isolation by flash chromatography on silica gel (eq. 1). The results of the silylcarbonylation of a variety of azaenynes **1** are summarized in Table 1.



(1)



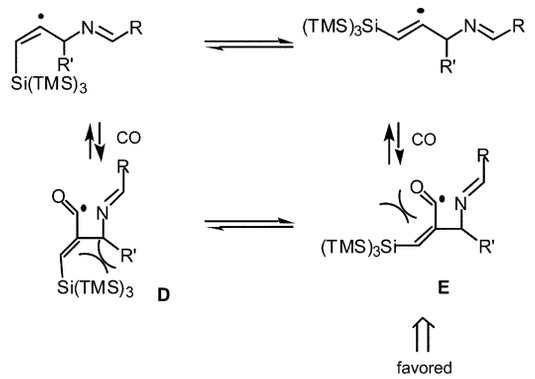
Scheme 2 Isomerization patterns for precursor radicals.

Using a similar set of reaction conditions, six-membered ring lactam **2e** was obtained from **1e** in 72% yield (run 7). The silylcarbonylation reactions of **1a** and **1f** also proceeded well to give four- and seven-membered ring lactams, **2a** and **2f**, respectively (runs 1 and 9). On the other hand, the corresponding eight-membered ring formation was inefficient with TTMSS, resulting in the formation of 20% yield of the lactam **2g** (run 11) where azaenyne **1g** was largely recovered unchanged.[13] The tendency for these reactions to favor the *E*-isomer during the formation of four to seven membered rings was consistently observed as depicted in Table 1 (runs 1, 5, 7 and 9), where the *E* : *Z* ratios are 85 : 15, 94 : 6, 100 : 0, and 85 : 15, respectively. This is in sharp contrast with the observation that the corresponding stannylcarbonylation of the same azaenynes using tributyltin hydride gave the analogous *Z*-products as the dominant stereoisomers in ratios of 32 : 68, 4 : 96, 0 : 100, and 19 : 81, respectively.[9]

Scheme 2 outlines a possible reaction course for the chemistry described herein, depicted using a model of the carbonylation–4-exo-cyclization sequence. Reversible addition of $(TMS)_3Si$ radicals to the terminus of the acetylene unit in the substrate will give rise to rapidly equilibrating vinyl radicals,[14] while the acyl radicals formed by the addition of these vinyl radicals to carbon monoxide may also beome involved in rapid diastereomeric equilibration *via* α-ketenyl radicals.[15,16] These radicals then undergo cyclization onto N–C double bonds to form the corresponding *E* and *Z* lactams. The *E*-preference for TTMSS reaction may be rationalized by the avoidance of steric congestion in **B**. In this regard, the *Z*-preference when G = $SnBu_3$ appears rather unusual, since the reaction sequence using tributyltin hydride would be expected to face similar steric congestion, although perhaps to a lesser extent. This result led us to postulate that stabilization through coordination of the carbonyl oxygen to the proximate tin atom, as depicted in hypervalent structure **C**, may be responsible for these observations. It is important to note that, to our knowledge, there is one example, which established a crystal structure of a pentacoordinated tetraorganyltin compound, 2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin, where the distance between tin and oxygen atoms is 2.781 Å.[17]

The effect of alkyl substitution at the propargylic position of the starting azaenyne was also examined using a system leading to β-lactams (runs 3 and 4). In these two cases, the *Z*-isomers were observed to be the major products. This is most likely to be due to $A^{1,3}$ strain between these alkyl substituents and the bulky $(TMS)_3Si$ group in structure **D** (Scheme 3).[18]

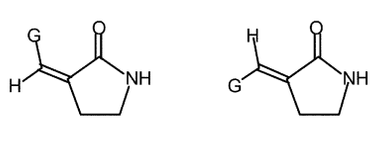
We also examined the cyclizative carbonylation of azaenynes using hexanethiol as a radical mediator and V-40 (1,1′-azobis(cyclohexane-1-carbonitrile)) as a radical initiator. The results are also shown in Table 1. Although the reaction requires rather harsh conditions to complete (110 °C (bath temperature)) and the yields are not as high as those involving tin and silicon, the corresponding α-thiomethylene lactams **3a**, **3d**, **3e**, and **3f** were obtained nevertheless (runs 2, 6, 8, and 10). The observed *E* : *Z* ratios of these α-thiomethylene lactams are



Scheme 3 Effect of alkyl substituent at allylic position.

86 : 14, 100 : 0, 100 : 0 and 85 : 15, clearly very similar to those observed for the TTMSS-mediated reactions. Unfortunately, thiocarbonylation of **1g** with hexanethiol gave a low yield of the eight-membered ring product **3g** (run 12), and the uncyclized aldehyde *via* thioformylation[19] was formed as the major product. In contrast, the formation of aldehydes is not observed in TTMSS-mediated reactions. Thus, an exceptionally rapid hydrogen abstraction of acyl radicals from thiols,[20] whose transition state would be expected to be influenced by polar effects competes effectively with the desired acyl radical cylization onto the N–C double bond.

In order to provide further insight into the factors governing the stabilities of the various *E* and *Z* isomers in this study, *Ab initio* and density functional (DFT) MO calculations were performed on the three sets of *E* and *Z* isomers of the five-membered ring lactam as model compounds (**5E** and **5Z**) (Fig. 1). The results of this study are summarized in Table 2.



5Z **5E**

Fig. 1 Model compounds **5Z** and **5E** (G = SnH_3, SiH_3, SMe).

For computational efficiency, H_3Sn, H_3Si, and CH_3S were employed as the substituents attached to the termini of the vinylic portion of these compounds. As a result of this, the calculations do not accurately model the steric factors associated with the substituents in the model study, but should nevertheless provide insight into electronic phenomena that may lead to the unexpected trends discussed above. In agreement with the experimental data, calculations at the B3LYP/DZP level of theory predict that the *Z*-form of the tin-containing compound (**5Z**, G = SnH_3) is *ca.*15 kJ mol^{-1} more stable than the corresponding *E* isomer (**5E**, G = SnH_3). In comparison, the energy difference between *Z* and *E* isomers of the silicon-containing structure is very small. This result does not argue against the argument presented in Scheme 2 that a stabilizing interaction

Table 2 Relative total energies of **5Z** and **5E** (values given in kJ mol^{-1})

G	Method	5Z	5E
SnH_3	RHF/DZP	−16.4	0.0
	B3LYP/DZP	−15.2	0.0
SiH_3	RHF/DZP	−1.0	0.0
	B3LYP/DZP	−0.4	0.0
SMe	RHF/DZP	0.0	−18.4
	B3LYP/DZP	0.0	−12.2

between the oxygen and tin atoms in **5Z** (G = SnH_3) would lead to preferential formation of the *Z*-form isomer in this case. On the other hand, the preference for the *E*-form observed for TTMSS reactions can be ascribed to a steric effect associated with the bulky $(TMS)_3Si$ group. As for sulfur-containing products, the calculations predict that the *E* isomer is strongly favored by about 12 kJ mol^{-1} over the *Z*-compound. Lone pair–lone pair repulsion between oxygen and sulfur is a possible rationale for the *E*-preference.

Mulliken population analysis provided by the B3LYP/DZP data for each of the *Z*-isomers under consideration affords further evidence in favor of this argument. In **5Z** (G = SnH_3), calculations predict a strong stabilizing (bonding) interaction between the tin and oxygen atoms that manifests itself in the short Sn–O separation of 2.79 Å (Fig. 2), significantly within the sum of the Van der Waals radii of the individual atoms (4.6 Å),[21] and a Mulliken bond population of 0.032, suggesting a bond strength of about 10–15% that of a tin-oxygen covalent bond. By contrast, the similar data for the silicon and sulfur containing species are 2.94 Å and 0.022 (5–10%), and 2.99 Å, and 0.011 (<5%), respectively. It is clear as a result of these calculations that there is a strong electronic preference for the *Z*-isomer when tin is involved in this chemistry, little electronic preference for either isomer when silicon is involved, resulting in steric factors dominating, while the sulfur analog strongly favours the *E*-isomer.

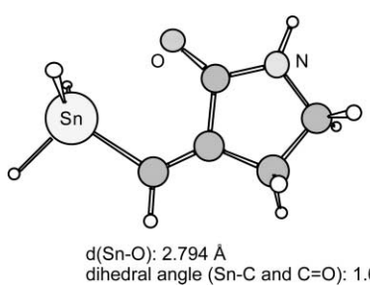


Fig. 2 Optimized structure of model compound **5Z** (G = SnH_3) on the B3LYP/DZP level of theory.

Conclusion

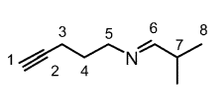
We have succeeded in expanding the cyclizative radical carbonylation chemistry of azaenynes to include TTMSS- and hexanethiol-mediated processes, in which the four- to seven-membered lactams were obtained through incorporation of carbon monoxide. The *E*-favoring diastereoselectivity in these systems is in sharp contrast to the *Z*-favoring selectivity observed previously in the analogous reactions with tributyltin hydride. Molecular orbital calculations of the five-membered products at the B3LYP/DZP level predict that *Z*-isomer is more stable than *E*-isomer when Sn is involved, and the *E*-isomer is more stable when sulfur is involved, in good agreements with the experimental results. Although significant energetic differences between *E* and *Z* isomers are not suggested for the silicon-containing products, pronounced steric effects associated with the bulky $(TMS)_3Si$ group may reasonably account for the origin of the *E*-selectivity observed for the α-silylmethylene lactams in this study. Mulliken population analysis provides further evidence in favor of this argument. Enantiopure 3-alkylpiperidines are potent pharmacores in medicinal chemistry and the recent work by Yue and Nugent[22] on Ir-catalyzed enantioselective hydrogenation of 3-alkylidene lactams is noteworthy. We believe that the present work which treats *E* : *Z* diastereoselective synthesis of α-heteroalkylidene lactams will hold promise to the next stage of enantioselective synthesis of 3-alkyl nitrogen-heterocycles.

Experimental

General

^{1}H NMR spectra were recorded with a JEOL FT-NMR JNM-270EX (270 MHz) spectrometer or JEOL FT-NMR JMN-ECP 500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) relative to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (δ 0.00 ppm) as internal standard. ^{13}C NMR spectra were recorded with a JEOL FT-NMR JMN 270EX (68 MHz) spectrometer or a JEOL FT-NMR JMN-ECP 500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. Infrared spectra were recorded with JASCO FT/IR-410 spectrometer, and absorptions were reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer or JEOL MS station MS-700 spectrometer. The products were purified by flash chromatography on silica gel (Fuji Silysia BW-300) and, if necessary, were further purified by recycling preparative HPLC (JAI LC-908) equipped with a GPC column using $CHCl_3$ as eluant. The signals in the ^{1}H and ^{13}C NMR spectra of new compounds were assigned with the aid of 2D-NMR (H–H COSY, and C–H COSY). *E* : *Z* configurations of **2a**, **2d**, and **2f** were determined by NOE. Vinylic protons in the *E*-isomers showed larger NOE than those in the *Z*-isomers. For example, (*E*)-**2a** provided 19.0% NOE between vinylic proton and ring protons while (*Z*)-**2a** showed 10.5% NOE between them. In these cases, vinylic protons of *E*-isomers resonate at lower field (6.76–6.18 ppm) than those of *Z*-isomers (6.05–5.69 ppm). Structures of other compounds (**2b**, **2c**, **2g**) were determined by comparing chemical shifts for their vinylic proton with those of the compounds whose structures were established by a NOE. Compound **2e**, which is obtained as a single isomer, displayed a small NOE (10.0%), and chemical shift of the vinyl proton at 7.17 ppm, supporting that the product has *Z*-configuration. Configuration of product **3g** (*E* or *Z*) was also established by NOE, and *E*–*Z* structures of compounds **3a**–**3f** were determined by referring to the chemical shifts observed for vinylic proton of **3g**.

Preparation of azaenyne 1e

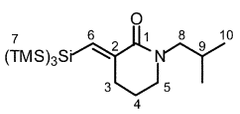


A mixture of 4-pentynylamine (11.1 mmol, 920 mg), isobutylaldehyde (22.3 mmol, 1.61 g), and K_2CO_3 (10 g) in Et_2O (50 mL) was stirred at room temperature for 12 h. After filtration, the solvent was evaporated. The residue was distilled under reduced pressure to give 1.21 g (69%) of **1e** (105 °C, 10 mmHg), ν_{max}(neat)/cm^{-1} 3308 (≡CH) and 1672 (C=N); δ_H (270 MHz; $CDCl_3$) 1.07 (6H, d, *J* 6.9, H-8), 1.82 (2H, quintet, *J* 6.9, H-4), 1.95 (1H, t, *J* 2.6, H-1), 2.20 (2H, dt, *J* 6.9 and 2.6, H-3), 2.40–2.44 (1H, m, H-7), 3.45 (2H, t, *J* 6.9, H-5) and 7.55 (1H, d, *J* 5.3, H-6); δ_C (68 MHz; $CDCl_3$) 15.76 (C-4), 19.26 (C-8), 29.04 (C-3), 33.89 (C-7), 59.28 (C-5), 68.55 (C-1), 3.63 (C-2) and 170.33 (C-6); *m*/*z* (EI)137 (M^+, 6%), 136 (21), 122 (100), 94 (38) and 67 (77) (Found: M^+ 137.1179. $C_9H_{17}N$ requires *M*, 137.1204).

Azaenynes **1a**, **1b**, **1c**, **1d**, **1f** and **1g** were prepared by a similar procedure from the corresponding amines and aldehydes.

Typical procedure for the silylcarbonylation of azaenynes: *N*-Isobutyl-3(*E*)-tris(trimethysilyl)silylmethylene-2-piperidinone 2e

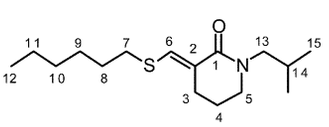
CAUTION: Carbon monoxide is a colourless, odourless, and highly toxic gas; all operations should be carried out in a fume hood with the utmost care. A magnetic stirring bar, AIBN (42.7 mg, 0.3 mmol), benzene (10 mL), $(TMS)_3SiH$ (285 mg, 1.1 mmol), and *N*-isopropilidene-4-pentenylamine (**1e**; 138 mg, 1 mmol) were placed in a 50 mL stainless autoclave lined with a glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 85 atm of CO and then heated at 85 °C for 8 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant hexane–EtOAc =19 : 1) to give 299 mg (72%) of **2e**.



Isolated as colourless oil, ν_{max}(neat)/cm^{-1} 1639 (C=O) and 1584 (C=C); δ_H (270 MHz; $CDCl_3$) 0.20 (27H, s, H-7), 0.91 (6H, d, *J* 6.6, H-10), 1.87 (2H, quintet, *J* 5.9, H-4), 2.06 (1H, tseptet, *J* 7.6 and 6.6, H-9), 2.56 (2H, dt, *J* 5.9 and 1.3, H-3), 3.24 (2H, d, *J* 7.6, H-8), 3.36 (2H, t, *J* 5.9, H-5) and 7.17 (1H, t, *J* 1.3, H-6); δ_C (68 MHz; $CDCl_3$) 1.26 (C-7), 20.24 (C-10), 23.45 (C-4), 26.65 (C-9), 31.54 (C-3), 49.22 (C-5), 55.67 (C-8), 132.15 (C-6), 144.22 (C-2) and 163.79 (C-1); *m*/*z* (EI) 398 ($M^+ - CH_3$, 2%), 340 (33), 266 (12), 224 (61), 73 (100); (Found: M^+, 413.2429. $C_{19}H_{43}NOSi_4$ requires *M*, 413.2422). NOE between H3 and H6: 10%.

Typical procedure for the thiocarbonylation of azaenynes: 3(*E*)-Hexylsulfanylmethylene-1-isobutyl-2-piperidinone 3e

A magnetic stirring bar, V-40 (48.9 mg, 0.2 mmol), benzene (50 mL), hexylmercaptane (70.9 mg, 0.6 mmol), and *N*-isopropilidene-4-butylamine (**1e**; 74 mg, 0.5 mmol) were placed in a 50 mL stainless autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 85 atm of CO and then heated at 110 °C for 12 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant hexane–Et_2O = 1 : 1) to give 86.1mg (72%) of **3e**.



Isolated as colourless oil, ν_{max}(neat)/cm^{-1} 1637 (C=O); δ_H (500 MHz; $CDCl_3$) 0.86–0.90 (9H, m, H-12, 15), 1.24–1.40 (6H, m, H-9, 10, 11), 1.67 (2H, quintet, *J* 7.6, H-8), 1.86 (2H, quintet, *J* 5.7, H-4), 1.98 (1H, septet, *J* 6.9, H-14), 2.40 (2H, dt, *J* 6.4 and 1.8, H-3), 2.80 (2H, t, *J* 7.3, H-7), 3.23 (2H, d, *J* 7.3, H-13), 3.31 (2H, t, *J* 5.7, H-5) and 7.51 (1H, t, *J* 1.8, H-6); δ_C (125 MHz; $CDCl_3$) 13.85 (C-12), 20.02 (C-15), 22.29 (C-4, 10 or 11), 22.35 (C-4, 10 or 11), 26.02 (C-3), 26.76 (C-14), 28.05 (C-9), 30.43 (C-8), 31.16 (C-10 or 11), 34.14 (C-7), 48.31 (C-5), 55.06 (C-13), 124.14 (C-2), 137.74 (C-6) and 163.16 (C-1); *m*/*z* (EI), 283 (M^+, 25%), 250 (28), 240 (67), 227 (43), 198 (100), 155 (37), 142 (37), 124 (26), 112 (14), 99 (24), 83 (24), 65 (18), 55 (50) (Found: M^+, 283.1963. $C_{16}H_{29}NOS$ requires *M*. 283.1970).

Computational chemistry

All *ab initio* and density functional (DFT) molecular orbital calculations were carried out using the Gaussian 98 program.[23] Geometry optimizations were performed using standard gradient techniques[24] at the SCF and B3LYP levels of theory. All calculations were performed using the previously published DZP basis set[25,26] as described by us.[27]

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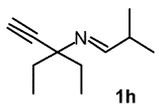
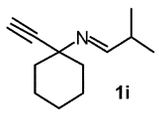


1h



1i

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