

Tin-Mediated Free-Radical Cyclization of β -Allenylbenzoyloximes

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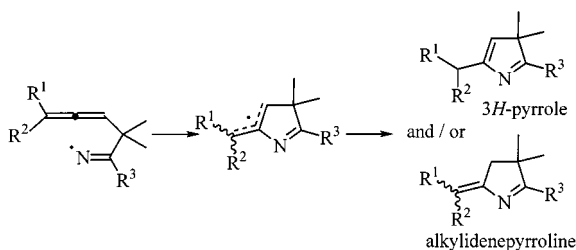
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A set of allene-tethered benzoyloximes (**5**) has been treated with $n\text{Bu}_3\text{SnH}$. Depending on their substitution pattern, a wide range of compounds has been obtained. If the stannyl radical adds on the allene, the C-centred radical thus formed undergoes either a 5-exo ring closure to give the cyclopentene derivatives **7** or a 6-endo ring closure onto the

N atom to give the dihydropyridines **8**. If the stannyl radical adds on the benzoyl moiety, an iminyl radical is formed which leads to the 3H-pyrroles **9** and the alkylidenepyrrolines **10**. Steric effects as well as polar effects are the factors governing the reaction course.

Introduction

In the last few decades many examples involving intramolecular addition of free radicals to carbon–carbon multiple bonds have been reported.^[1–4] Some papers dealing with an analogous addition to carbon–nitrogen multiple bonds have appeared as well.^{[5][6]} From this point of view, our group has already reported on the $n\text{Bu}_3\text{SnH}$ mediated free radical cyclization of allene tethered oxime ethers and hydrazones.^[7] Thus, we obtained five-membered carbocycles bearing a protected amino group and a vinylstannyl functionality. Recently, an increasing number of papers deals with the intramolecular addition of nitrogen-centred radicals onto various acceptors.^{[5][8]} In this area, Zard and co-workers have obtained pyrrolines using an iminyl radical, easily produced by the tributylstannane reduction of alkene-tethered benzoyloximes.^[9] The use of this method with our allenic compounds would be a good way of obtaining stable 3H-pyrroles or alkylidenepyrrolines (see Scheme 1).



Scheme 1. Reaction of β -allenyliminyl radicals

In this paper, we now describe the first results obtained in the tributylstannane-mediated cyclization of allene-tethered benzoyloximes.

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Results and Discussion

The structure and functionality of these allenylbenzoyloximes raise an interesting problem: Two principal positions are available for attack by stannyl radicals. The first one is the oxygen atom of the carbonyl group that causes the formation of the required iminyl radical by addition of the stannyl radical. The second position is the allene functionality. Consequently, the behaviour of allenylbenzoyloximes towards stannyl radicals strongly depends on the relative kinetics of the tin radical addition to either position. So a systematic structure-reactivity analysis seems to be necessary to determine the factors governing the reaction pathway.

Synthesis of the Radical Precursors **5**

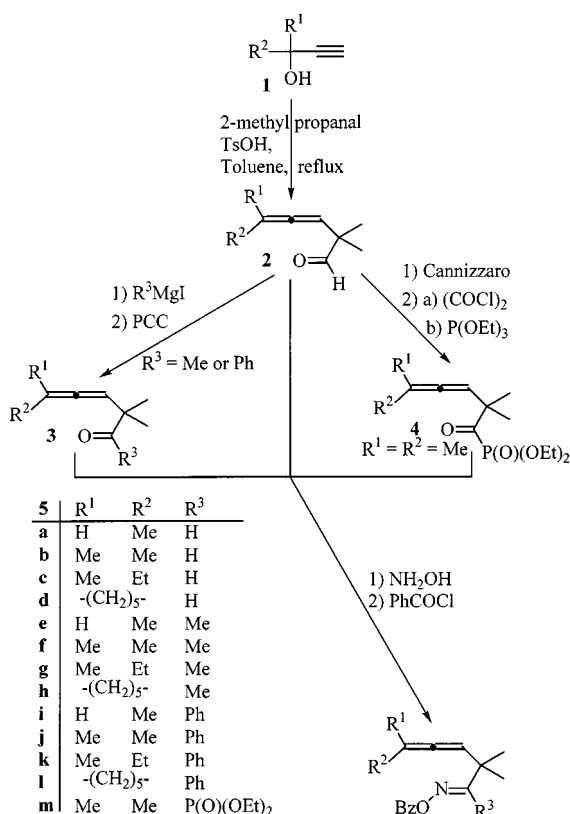
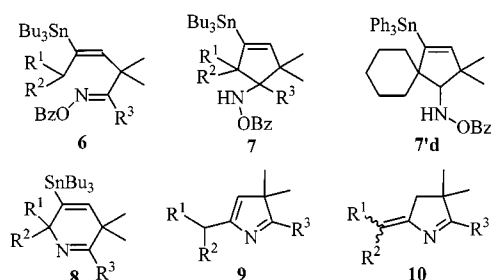
A set of β -allenylbenzoyloximes was therefore prepared in a few steps starting from the corresponding propargylic alcohols **1** according to Scheme 2.

The β -allenylaldehydes **2** can easily be obtained from the alcohols **1**.^[10] Grignard reagent addition to **2**, followed by PCC oxidation^[11] of the crude alcohols affords the ketones **3**. Cannizzaro reaction with **2b** ($R^1 = R^2 = \text{CH}_3$) gives the corresponding β -allenyl acid^[10] which is converted into the acid chloride. Compound **4** is then obtained by Arbusov reaction^[12] of this acid chloride with triethyl phosphite. These compounds, **2–4**, can be submitted to oximation and benzoylation to give the β -allenylbenzoyloximes **5**.

Reaction of Tin Hydrides with the Radical Precursors **5**

Depending on their substitution pattern, compounds **5** led to different products (**6–10**; Figure 1) when they were submitted to the action of tin hydrides in radical conditions.

As it seems to be of some importance in the product distribution, we are going to discuss our results relative to the nature of the R^3 substituent. For $R^3 = \text{H}$, **5a–d** were prone to give the corresponding nitrile and benzoic acid, when they were heated under reflux in cyclohexane. For that reason, we treated these compounds with $n\text{Bu}_3\text{SnH}$ or Ph_3SnH

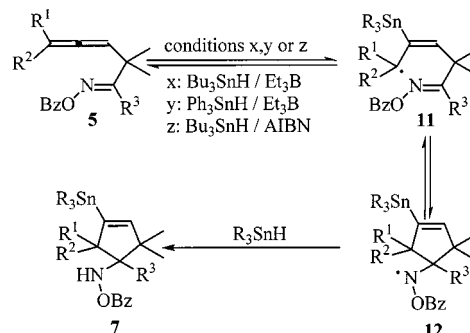
Scheme 2. Synthesis of radical precursors **5a–m**Figure 1. Products obtained from the tin hydride reaction on **5**

(in one case) in the presence of triethylborane, to avoid this thermal decomposition.^[13] Thereby, as it is shown in Table 1, we only obtained the five-membered cyclized products **7a–d** and **7'd**.

Table 1. Tin hydride reaction of radical precursors **5a–h**

5	Reaction conditions	Reaction time [h]	Recovered 5 (%)	Yield of 7 (%)
a	<i>n</i> Bu ₃ SnH/Et ₃ B, 25 °C	48	13	71
b	<i>n</i> Bu ₃ SnH/Et ₃ B, 40 °C	48	22	75
c	<i>n</i> Bu ₃ SnH/Et ₃ B, 40 °C	48	20	65
d	<i>n</i> Bu ₃ SnH/Et ₃ B, 40 °C	48	31	48
d	Ph ₃ SnH/Et ₃ B, 25 °C	2.4		91 (7'd)
e	<i>n</i> Bu ₃ SnH/AIBN, 80 °C	8		81
f	<i>n</i> Bu ₃ SnH/AIBN, 80 °C	8		75
g	<i>n</i> Bu ₃ SnH/AIBN, 80 °C	48		
h	<i>n</i> Bu ₃ SnH/AIBN, 80 °C	48		

With the particular substitution pattern of the allenes we used, the stannyl radical adds only onto the diagonal carbon atom (see Scheme 3). The subsequent 5-*exo-trig* cyclization onto the C=N bond, and H abstraction from tin hydride by the obtained aminyl radical affords **7**.

Scheme 3. Mechanistic pathway for obtaining **7**

These reactions were relatively slow when *n*Bu₃SnH was used and were stopped after 48 hours (Table 1). The bulkier R¹ and R² the lower the yield of cyclized product **7**. For **5a** and **5c** the cyclization afforded an unseparable mixture of two stereoisomers (69:31 and 75:25, respectively). The major isomer in both cases is where the methyl group and the amino group are *cis*.^[14] The use of Ph₃SnH was tested on **5d** and allowed us to obtain **7'd** in excellent yield despite the high steric hindrance of R¹ and R². Actually, Ph₃SnH is a better reducing agent than *n*Bu₃SnH.^[15] Thus, it likely means that the stannyl radical addition onto the allene, and the 5-*exo* cyclization are both reversible processes, the H abstraction being the kinetically determining step. It is worthy to note that no product resulting from the formation of an iminyl radical has been detected in the crude products.

For R³ = CH₃ (**5e–h**), we used *n*Bu₃SnH/AIBN in refluxing cyclohexane (Table 1). For **5e** and **5f** we obtained the vinyltin derivatives **7e–f** in good yield; the carbocycle **7e** was isolated as an unseparable mixture of two stereoisomers (60:40) in which the major isomer has the methyl group and the amino function in *cis* relative conformation.^[14] Compared with the behaviour of **5f**, the corresponding allyllallene (2,3,3,6-tetramethylhepta-1,4,5-triene) gave 6-*endo* cyclization as the major process.^[16] As we have discussed earlier, however,^[17] this difference in the two behaviours is not surprising when the polarity of the C=N bond is considered.

With **5g** and **5h**, no cyclization occurred. In fact the ¹H-NMR analysis of the crude products did not show any signal in the 3–6 ppm area; indicating that neither **7g–h** nor **8g–h** nor **6g–h** were significantly present in the mixtures. In both cases, starting material was totally degraded after 48 hours and gave an unidentifiable mixture of compounds. The use of Ph₃SnH instead of *n*Bu₃SnH did not give better results.

For R³ = Ph (**5i–l**) and, in one case, R³ = P(O)(OEt)₂ (**5m**), the reaction evolution is slightly more complex. De-

pending on the substituents R^1 and R^2 a mixture of **6** and **7** or a mixture of **8**, **9**, and **10** was obtained (Table 2).

Table 2. Reaction of radical precursors **5i–m** with tributyltin hydride (AIBN, c -C₆H₁₂, reflux)

5	Reaction time [h]	Recovered 5 (%)	% of isolated products			
			6	7	8	9 + 10
i	13		19	44		
j	5.5				82	< 10
k	30				42	48
l	20	12			17	43
m	6				55	

Submitted to our experimental conditions, the radical precursor **5i** gave a small amount of the linear product **6i** (19%) and the five-membered cyclized product **7i** (44%). The latter was isolated as a mixture of two stereoisomers in a 9:1 ratio in which the major isomer has the methyl group and the amino function in *cis* relative orientation.^[14]

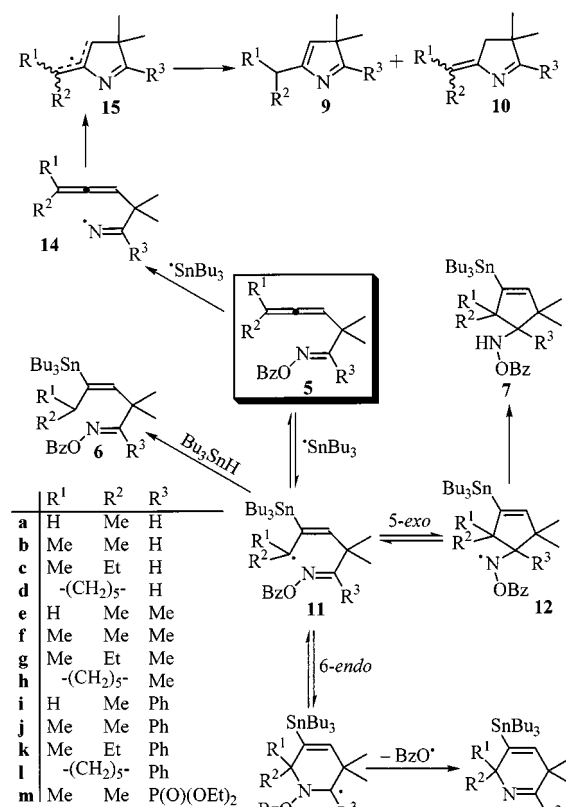
For **5j–l**, a mixture of **8j–l**, **9j–l**, and **10j–l** were obtained. In these three examples, **9** and **10** were obtained in approximately equal ratio. We must observe that the yield of **8** decreases when the steric hindrance of R^1 and R^2 increases; at the same time, the yield of both **9** and **10** increases. When $R^3 = \text{P(O)(OEt)}_2$ (**5m**), compound **8m** was the sole product of the reaction. It was obtained in a quasi-quantitative yield for the crude product. So, the 55% yield in isolated **8m** seems to be the result of its degradation on silica gel during its purification.

Discussion

As is shown in Tables 1 and 2, a wide range of products can be obtained from the reaction of tin hydride on radical precursors **5a–m**. Depending on the substitution pattern of the starting compound, **5**, cyclopentene derivatives **7**, 2,5-dihydropyridines **8**, 3*H*-pyrroles **9**, and alkylidenepyrrroles **10** are the main products of the reaction. In Scheme 4 we show a tentative mechanism to explain all our results.

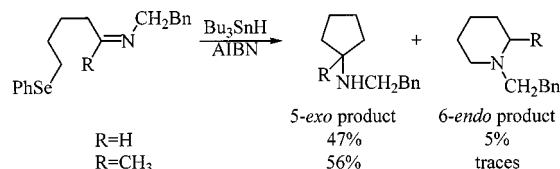
Starting from **5**, the addition of the stannyl radical to the allene seems to be the favoured process. The obtained radical **11** undergoes a 5-*exo* cyclization leading to **7** when the substitution pattern is not hindered as in the case of **5a–f** (Table 1) and **5i** (Table 2). In this latter case the bulky phenyl group slows down the 5-*exo* cyclization, thus the H abstraction from tin hydride can compete to give **6i**, since the secondary radical **11i** is not too bulky. For **5j–m** the radical **11** undergoes a 6-*endo* cyclization onto the nitrogen atom. Subsequent debenzoylation from the so-obtained radical **13** leads to the 2,5-dihydropyridines **8j–m**. When $R^3 = \text{Ph}$ (**5j–l**), the formation of iminyl radical **14** competes with the formation of **13** and a mixture of **9** and **10** is also obtained (via the allylic radical **15**).

Starting from **11**, the two possible courses of the reaction, 5-*exo* or 6-*endo* ring closure, deserve some comments. To our knowledge, only one case of 6-*endo* ring closure of a C-



Scheme 4. Tentative mechanism for obtaining compounds **6–10**

centred radical onto a nitrogen atom of a C=N bond has been reported (Scheme 5).^[18]



Scheme 5. Radical cyclization of 5-benzeneselenenylalkylimines

In this case, the 5-*exo* ring closure is normally the major process, for stereoelectronic effects as well as for polar effects.^{[18][19]} With a methyl group on C-1, the increasing steric hindrance is not enough to slow down the 5-*exo* ring closure, contrary to the 5-hexenyl radical cyclization.^[20] On the other hand, the increasing polarity of the C=N bond due to the methyl group favours this cyclization process. In our case, the formation of **12** in a 5-*exo* cyclization mode would be also the favoured process. That is indeed the case starting from **5a–f** and **5i**. Starting from **5g–h**, the overall substitution hindrance is probably too large and slows down the 5-*exo* ring closure as it is normally expected; but that does not allow the 6-*endo* ring closure to be competitive. It means that the formation of **8j–m** by an effective 6-*endo* ring closure of the nucleophilic C-centred radical **11** onto the nitrogen atom of the C=N bond cannot only be explained by stereoelectronic or steric effects as is the case

in 5-hexenyl radical.^[20] Similar observations have been reported by Komatsu^[21] in the ring closure of 6-aza-7-heptadien-2-yl system. Moreover, as we have previously shown,^[17] that cannot be explained by π delocalization of radical **13**. On the other hand, it is well-known that the attack of a nucleophilic radical onto an olefin is strongly favoured by the polar effect induced by an electron-withdrawing substituent at the carbon atom which is not attacked (β -substituent effect).^[22] From a similar point of view, we assume that the presence of an electron-withdrawing group [$R^3 = \text{Ph}$, $\text{P}(\text{O})(\text{OEt})_2$] at the carbon atom of the carbon–nitrogen double bond is necessary to make the nitrogen atom more attractive towards nucleophilic radicals.

Conclusion

In summary, in this work, we have shown that the action of tributyltin hydride on a wide range of β -allenylbenzoyloximes mainly occurs on the allenic sp-carbon atom. Depending on the type of substitution on the carbon atom of the oxime function, the reaction gives either the cyclopentene derivatives **7** or 2,5-dihydropyridines **8**, both bearing a tributyltin group. Starting from the unsubstituted or methyl-substituted benzoyloximes **5**, cyclopentenones **7** are obtained from a 5-*exo* ring closure. With methyl-substituted benzoyloximes, this reaction fails when the allene is overcrowded. When the benzoyloxime substituent is an electron-withdrawing group [Ph , $\text{P}(\text{O})(\text{OEt})_2$], a 6-*endo* ring closure takes place onto the nitrogen atom of the $\text{C}=\text{N}$ bond, leading to the 2,5-dihydropyridines **8**. Iminyl radical formation competes with the latter process when the steric hindrance at the terminal, trigonal carbon atom increases. In this way, 3*H*-pyrroles **9** and alkylidenepyrrolines **10** are obtained. At last, we succeeded in chemoselective formation of **9** and **10** using a radical precursor other than **5**.^[23]

Experimental Section

Presented are selected data; a complete Experimental Section is available on the WWW under <http://www.wiley-vch.de/home/eurjoc> or from the author.

General: Melting points are uncorrected. – ^1H - and ^{13}C - NMR spectra were performed in CDCl_3 with tetramethylsilane as internal reference, and recorded with Bruker AC 200 and AMX 400 spectrometers. – IR: Mattson 1000 FT-IR. – Merck silica gel 60 (230–400 mesh) was used for column chromatography. – Solvents and reagents were purified according to standard laboratory techniques. – Abbreviation used: AIBN = 2,2'-azobis(2-methylpropanitrile).

General Procedure for the Preparation of the β -Allenyl Ketones **3:** The β -allenyl ketones **3** were obtained in the standard manner, first by the action of methyl- or phenylmagnesium iodide on the β -allenyl aldehydes **2**,^[10] and then by oxidation of the resulting β -allenyl alcohols by PCC.^[11] The crude ketones were purified by silica-gel column chromatography (eluent: Et_2O /pentane).

3,3,6-Trimethylhepta-4,5-dien-2-one (3f): 66% yield, colourless oil. – IR (neat): $\tilde{\nu} = 1965 \text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{C}$), 1710 (C=O) . – ^1H NMR

(200 MHz): $\delta = 1.16$ [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.70 [d, $J = 2.8 \text{ Hz}$, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 2.13 (s, 3 H, $\text{CH}_3\text{C}=\text{O}$), 4.98 (m, $J = 2.8 \text{ Hz}$, 1 H, $\text{CH}=\text{C}$) – ^{13}C NMR (50 MHz): $\delta = 19.8$ (CH_3), 23.9 (CH_3), 24.5 (CH_3), 48.1 [$\text{C}(\text{CH}_3)_2$], 95.3 ($\text{C}=\text{C}=\text{CH}$), 97.9 ($\text{C}=\text{C}=\text{CH}$), 200.8 ($\text{C}=\text{C}=\text{CH}$), 210.6 ($\text{C}=\text{O}$).

2,2,5-Trimethyl-1-phenylhexa-3,4-dienone (3j): 64% yield, colourless oil. – IR (CCl_4): $\tilde{\nu} = 1965 \text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{C}$), 1680 ($\text{C}=\text{O}$). – ^1H NMR (200 MHz): $\delta = 1.37$ [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.65 [d, $J = 2.9 \text{ Hz}$, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 5.23 (m, $J = 2.9 \text{ Hz}$, 1 H, $\text{CH}=\text{C}$), 7.36 – 7.46 (m, 3 H, Ph), 7.92 – 7.98 (m, 2 H, Ph). – ^{13}C NMR (50 MHz): $\delta = 20.0$ (CH_3), 26.8 (CH_3), 48.1 [$\text{C}(\text{CH}_3)_2$], 96.9 ($\text{C}=\text{C}=\text{CH}$), 99.0 ($\text{C}=\text{C}=\text{CH}$), 127.8 , 129.3 and 131.5 (CH, Ph), 137.1 (C, Ph), 200.9 ($\text{C}=\text{C}=\text{CH}$), 205.0 ($\text{C}=\text{O}$).

Preparation of the β -Allenyl Phosphonate **4:** Under argon, 20 mL of a 2 M solution of oxalyl chloride in CH_2Cl_2 was added to a solution of the β -allenyl acid (3.08 g, 20 mmol)^[10] in 5 mL of anhydrous CH_2Cl_2 at 0°C . The reaction mixture was stirred at 20°C for 1 h, and excess oxalyl chloride was then removed under reduced pressure. The residual acid chloride was cooled to 0°C and of $\text{P}(\text{OEt})_3$ (3.5 mL, 20 mmol) was added dropwise. The reaction mixture was stirred at 20°C for 1 h. Distillation of the mixture gave **4**.

1-Diethylphosphonato-2,2,5-trimethylhexa-3,4-dienone (4): 52% yield, colourless oil, b.p. 105 – $110^\circ\text{C}/0.1 \text{ Torr}$. – ^1H NMR (200 MHz): $\delta = 1.26$ [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.28 and 1.29 (2t, $J = 7.2 \text{ Hz}$, 6 H, OCH_2CH_3), 1.64 [d, $J = 2.9 \text{ Hz}$, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 4.13 and 4.14 (2quin, $J = 7.2 \text{ Hz}$, 4 H, OCH_2CH_3), 5.18 (m, 1 H, $\text{CH}=\text{C}$). – ^{13}C NMR (50 MHz): $\delta = 16.2$ and 16.3 (OCH_2CH_3), 20.1 (CH_3), 23.3 (CH_3), 50.1 [d, $J = 55.4 \text{ Hz}$, $\text{C}(\text{CH}_3)_2$], 63.3 and 63.4 (OCH_2CH_3), 92.7 ($\text{C}=\text{C}=\text{CH}$), 98.8 ($\text{C}=\text{C}=\text{CH}$), 202.4 ($\text{C}=\text{C}=\text{CH}$), 211.7 (d, $J = 154.0 \text{ Hz}$, $\text{C}=\text{O}$).

General Procedure for the Preparation of the β -Allenylbenzoyloximes **5:** To a stirred mixture of CH_2Cl_2 (10 mL), pyridine (10 mL), and hydroxylamine hydrochloride (2.09 g, 30 mmol) was added 4-Å molecular sieves and 15 mmol of **2**, **3**, or **4**. The reaction was monitored by TLC (for the compounds **3a–h** the reaction was completed after 1 h; for the compounds **3i–m** and **4** the reaction mixture was heated under reflux overnight). The mixture was diluted with 70 mL of Et_2O , filtered, and washed with 40 mL of water. The organic layer was then extracted with a 5% aqueous CuSO_4 solution to remove pyridine. The solvent was dried with MgSO_4 and concentrated under reduced pressure giving crude β -allenyl oximes. To a solution of the so-obtained oximes (10 mmol) in a mixture of 20 mL of Et_2O and 2 mL of pyridine, 2 mL of benzoyl chloride was added dropwise. After 2 h, 3 mL of water and then 70 mL of an aqueous saturated Na_2CO_3 solution were added. The reaction mixture was stirred overnight. The aqueous phase was extracted with Et_2O and the combined organic layers were washed with a 5% aqueous CuSO_4 solution. The solvent was dried with MgSO_4 and concentrated under reduced pressure giving crude β -allenylbenzoyloximes which were purified by silica-gel column chromatography (eluent: Et_2O /pentane).

2,2,5-Trimethylhexa-3,4-dienal O-Benzoyloxime (5b): 75% yield, white crystals (pentane), m.p. 32 – 34°C . – IR (KBr): $\tilde{\nu} = 1972 \text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{C}$), 1735 ($\text{C}=\text{O}$). – ^1H NMR (200 MHz): $\delta = 1.31$ [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.70 [d, $J = 2.9 \text{ Hz}$, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 5.02 (sept, $J = 2.9 \text{ Hz}$, 1 H, $\text{CH}=\text{C}$), 7.39 – 7.57 (m, 3 H, Ph), 7.75 (s, 1 H, CHN), 8.02 – 8.07 (m, 2 H, Ph). – ^{13}C NMR (50 MHz): $\delta = 20.5$ (CH_3), 25.3 (CH_3), 38.6 [$\text{C}(\text{CH}_3)_2$], 95.6 ($\text{C}=\text{C}=\text{CH}$), 97.0 ($\text{C}=\text{C}=\text{CH}$), 128.0 , 128.9 and 133.1 (CH, Ph), 131.1 (C, Ph), 164.1 ($\text{C}=\text{O}$), 165.4 ($\text{HC}=\text{N}$), 200.1 ($\text{C}=\text{C}=\text{CH}$). – $\text{C}_{16}\text{H}_{19}\text{NO}_2$ (257.33): calcd. C 74.68, H 7.44, N 5.44; found C 74.66, H 7.47, N 5.36.

3,3,6-Trimethylhepta-4,5-dien-2-one *O*-Benzoyloxime (5f): 76% yield, white crystals (pentane), m.p. 47–48 °C. – IR (KBr): $\tilde{\nu}$ = 1967 cm^{-1} (C=C=C), 1745 (C=O). – ^1H NMR (200 MHz): δ = 1.32 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.71 [d, J = 2.8 Hz, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 2.04 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 4.99 (sept, J = 2.8 Hz, 1 H, $\text{CH}=\text{C}$), 7.44–7.56 (m, 3 H, Ph), 8.02–8.07 (m, 2 H, Ph). – ^{13}C NMR (50 MHz): δ = 13.1 ($\text{N}=\text{CCH}_3$), 20.4 (CH_3), 25.4 (CH_3), 42.7 [$\text{C}(\text{CH}_3)_2$], 96.2 (C=C=CH), 98.4 (C=C=CH), 128.4 129.4 and 133.0 (CH, Ph), 163.8 (C=O), 171.7 (C=N), 201.0 (C=C=CH). – $\text{C}_{17}\text{H}_{21}\text{NO}_2$ (271.36): calcd. C 75.25, H 7.80, N 5.16; found C 75.24, H 7.68, N 5.14.

2,2,5-Trimethyl-1-phenylhexa-3,4-dienone *O*-Benzoyloxime (5j): 66% yield, white needles (pentane), m.p. 104–106 °C. – IR (KBr): $\tilde{\nu}$ = 1965 cm^{-1} (C=C=C), 1753 (C=O). – ^1H NMR (200 MHz): δ = 1.38 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.59 [d, J = 2.8 Hz, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 5.12 (sept, J = 2.8 Hz, 1 H, $\text{CH}=\text{C}$), 7.15–7.60 (3 m, 10 H, Ph). – ^{13}C NMR (50 MHz): δ = 20.2 (CH_3), 26.1 (CH_3), 42.7 [$\text{C}(\text{CH}_3)_2$], 96.2 (C=C=CH), 98.7 (C=C=CH), 127.2 127.7 128.2 128.3 129.2 and 129.4 (CH, Ph), 132.9 and 133.5 (C, Ph), 163.7 (C=O), 174.0 (C=N), 201.4 (C=C=CH). – $\text{C}_{22}\text{H}_{23}\text{NO}_2$ (333.43): calcd. C 79.25, H 6.95, N 4.20; found C 79.18, H 6.95, N 4.12.

1-Diethylphosphonato-2,2,5-trimethylhexa-3,4-dienone *O*-Benzoyloxime (5m): 23% yield, colourless oil. – ^1H NMR (200 MHz): δ = 1.22 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.46 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.67 [d, J = 2.8 Hz, 6 H, $(\text{CH}_3)_2\text{C}=\text{C}$], 4.13 (m, 4 H, OCH_2CH_3), 5.40 (m, J = 2.8 Hz, 1 H, $\text{CH}=\text{C}$), 7.40–7.56 (m, 3 H, Ph), 8.14–8.19 (m, 2 H, Ph). – ^{13}C NMR (50 MHz): δ = 16.3 and 16.4 (OCH_2CH_3), 18.6 (CH_3), 26.5 (CH_3), 26.6 (CH_3), 43.3 (d, J = 21.1 Hz, [$\text{C}(\text{CH}_3)_2$], 62.6 and 62.7 (OCH_2CH_3), 95.5 (C=C=CH), 98.7 (C=C=CH), 128.6 130.1 and 133.5 (CH, Ph), 134.6 (C, Ph), 163.2 (C=O), 166.8 (d, J = 141.9 Hz, C=N), 201.6 (C=C=CH). – $\text{C}_{20}\text{H}_{28}\text{NO}_5\text{P}$ (393.42): calcd. C 61.06, H 7.17, N 3.56; found C 61.00, H 7.11, N 3.47.

General Procedure for the Tin-Mediated Radical Cyclization of the Compounds 5a–d (Table 1): A hexane solution of Et_3B (1.0 mL, 1.0 mmol) and 20 mL of air were added portionwise for 48 h to a solution of tin hydride (1.2 mmol) and **5a–d** (1.0 mmol) in cyclohexane (50 mL) under argon. The solvent was evaporated under reduced pressure and the crude mixture was purified by silica-gel column chromatography (eluent: Et_2O /pentane).

4-(Benzoyloxyamino)-3,3,5,5-tetramethyl-1-(tri-*n*-butylstannyl)cyclopentene (7b): 75% yield, colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1721 cm^{-1} (C=O). – ^1H NMR (200 MHz): δ = 0.83–0.96 (m, 15 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.08 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.26–1.54 (m, 12 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.25 (d, J = 7.4 Hz, 1 H, CHNH), 5.48 (s, 1 H, $\text{CH}=\text{C}$), 7.41–7.57 (m, 3 H, Ph), 8.00–8.05 (m, 2 H, Ph), 8.18 (d, J = 7.4 Hz, 1 H, CHNH). – ^{13}C NMR (50 MHz): δ = 9.7 (SnCH_2), 13.7 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 23.3 (CH_3), 24.0 (CH_3), 27.4 (CH_2), 29.2 (CH_2), 30.2 (CH_3), 31.1 (CH_3), 49.2 [$\text{C}(\text{CH}_3)_2$], 53.3 [$\text{C}(\text{CH}_3)_2$], 77.0 (CHNH), 128.6 129.2 and 133.2 (CH, Ph), 128.7 (C, Ph), 148.8 ($\text{CH}=\text{C}$), 151.1 ($\text{CH}=\text{C}$), 166.5 (C=O). – $\text{C}_{28}\text{H}_{47}\text{NO}_2\text{Sn}$ (548.38): calcd. C 61.33, H 8.64, N 2.55; found C 61.38, H 8.59, N 2.54.

General Procedure for the Tin-Mediated Radical Cyclization of the Compounds 5e–m (Tables 1 and 2): Bu_3SnH (1.2 equiv.) and AIBN (0.2 equiv.) were added to a cyclohexane solution (0.02 M) of the compounds **5e–m**. After this solution was degassed with a stream of argon, the mixture was heated under reflux, and monitored by TLC until the starting material had disappeared. After evaporation of the solvent, the crude mixture was purified by silica-gel column chromatography (Et_2O /pentane starting from **5e–i**; CH_2Cl_2 /ethyl acetate starting from **5m**).

4-(Benzoyloxyamino)-3,3,4,5,5-pentamethyl-1-(tri-*n*-butylstannyl)cyclopentene (7f): Obtained from **5f** in 75% yield, colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1751 cm^{-1} (C=O). ^1H NMR (200 MHz): δ = 0.83–0.93 (m, 15 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.08 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.24–1.52 (m, 12 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.44 (s, 1 H, $\text{CH}=\text{C}$), 7.39–7.56 (m, 3 H, Ph), 7.95–8.00 (m, 2 H, Ph), 8.04 (s, 1 H, Ph). – ^{13}C NMR (50 MHz): δ = 10.0 (SnCH_2), 13.7 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.8 (CH_3), 25.5 (CH_3), 26.2 (CH_3), 27.4 (CH_2), 29.2 (CH_2), 52.1 [$\text{C}(\text{CH}_3)_2$], 56.3 [$\text{C}(\text{CH}_3)_2$], 70.7 (CHNH), 128.6 129.2 and 133.1 (CH, Ph), 128.7 (C, Ph), 148.5 ($\text{CH}=\text{C}$), 150.4 ($\text{CH}=\text{C}$), 166.4 (C=O). – $\text{C}_{29}\text{H}_{49}\text{NO}_2\text{Sn}$ (562.41): calcd. C 61.93, H 8.78, N 2.49; found C 61.85, H 8.83, N 2.45.

Cyclization of **5i** gave a mixture of **6i** and **7i**.

2,2-Dimethyl-1-phenyl-4-(tri-*n*-butylstannyl)hex-3-enone *O*-Benzoyloxime (6i): 19% yield, colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1719 cm^{-1} (C=O). – ^1H NMR (400 MHz): δ = 0.80–1.00 (m, 15 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.24–1.33 (m, 6 H, CH_2), 1.41–1.47 (m, 6 H, CH_2), 1.50 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 2.62 (qd, J = 7.5 Hz and 2.2 Hz, 2 H, CH_2CH_3), 5.30 (d, J = 2.2 Hz, 1 H, $\text{CH}=\text{C}$), 7.17–7.62 (m, 10 H, Ph). – ^{13}C NMR (100 MHz): δ = 10.1 (SnCH_2), 13.7 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 14.7 (CH_3), 26.8 (CH_2), 27.4 (CH_2), 28.4 (CH_3), 29.1 (CH_2), 44.9 [$\text{C}(\text{CH}_3)_2$], 127.5 127.6 128.3 129.4 and 132.8 (CH, Ph), 129.3 and 134.0 (C, Ph), 142.3 ($\text{CH}=\text{C}$), 153.8 ($\text{CH}=\text{C}$), 163.8 (C=O), 173.8 (C=N). – $\text{C}_{33}\text{H}_{49}\text{NO}_2\text{Sn}$ (610.45): calcd. C 64.93, H 8.09, N 2.29; found C 65.01, H 8.11, N 2.26.

4-(Benzoyloxyamino)-3,3,5-trimethyl-4-phenyl-1-(tri-*n*-butylstannyl)cyclopentene (7i): 44% yield, pale yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). – The ^1H -NMR and ^{13}C -NMR spectra were recorded on a mixture of both isomers (9:1 ratio). Only the major isomer could be fully described. Major isomer: ^1H NMR (200 MHz): δ = 0.56 (s, 3 H, CH_3), 0.85–0.96 (m, 15 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.19 [d, J = 7.4 Hz, 3 H, $\text{CH}(\text{CH}_3)$], 1.21–1.36 (m, 6 H, CH_2), 1.35 (s, 3 H, CH_3), 1.37–1.51 (m, 6 H, CH_2), 3.77 [qd, J = 7.4 Hz and 2.3 Hz, 1 H, $\text{CH}(\text{CH}_3)$], 5.70 (d, J = 2.3 Hz, 1 H, $\text{CH}=\text{C}$), 7.25–7.79 (3m, 10 H, Ph), 8.16 (s, 1 H, NH). – ^{13}C NMR (50 MHz): δ = 9.6 (SnCH_2), 13.8 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 15.5 (CH_3), 22.7 (CH_3), 26.2 (CH_3), 27.4 (CH_2), 29.3 (CH_2), 51.1 (CH), 53.3 [$\text{C}(\text{CH}_3)_2$], 76.9 (CNH), 127.1 127.6 128.0 128.4 129.2 and 132.9 (CH, Ph), 128.9 and 140.5 (C, Ph), 145.1 ($\text{CH}=\text{C}$), 150.1 ($\text{CH}=\text{C}$), 165.7 (C=O). – Minor isomer: ^1H NMR (200 MHz) (incomplete description): δ = 3.26 [qd, J = 7.2 Hz and 2.8 Hz, 1 H, $\text{CH}(\text{CH}_3)$], 5.82 (d, J = 2.8 Hz, 1 H, $\text{CH}=\text{C}$). – ^{13}C NMR (50 MHz) (incomplete description): δ = 9.8 (SnCH_2), 13.8 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 27.4 (CH_2), 29.3 (CH_2), 54.3 (CH), 78.8 (CNH), 133.2 (CH, Ph), 139.8 (C, Ph), 146.6 ($\text{CH}=\text{C}$), 152.4 ($\text{CH}=\text{C}$), 166.3 (C=O). – $\text{C}_{33}\text{H}_{49}\text{NO}_2\text{Sn}$ (610.45): calcd. C 64.93, H 8.09, N 2.29; found C 64.89, H 8.06, N 2.26.

Cyclization of **5j** afforded a mixture of **8j**, **9j**, and **10j**.

2,2,5,5-Tetramethyl-6-phenyl-3-(tri-*n*-butylstannyl)-2,5-dihydropyridine (8j): 82% yield, colourless oil. – IR (CCl_4): $\tilde{\nu}$ = 1679 cm^{-1} (C=N). – ^1H NMR (400 MHz): δ = 0.88–0.97 (m, 15 H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.14 (s, 6 H, CH_3), 1.31–1.38 (m, 6 H, CH_2), 1.32 (s, 6 H, CH_3), 1.47–1.55 (m, 6 H, CH_2), 5.55 (s, 1 H, $\text{CH}=\text{C}$), 7.30 (m, 5 H, Ph). – ^{13}C NMR (100 MHz): δ = 10.5 (SnCH_2), 13.7 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 27.4 (CH_2), 28.7 (CH_3), 29.1 (CH_2), 32.0 (CH_3), 35.0 (C=C=N), 60.5 (C=N=C), 127.6 127.8 and 127.9 (CH, Ph), 141.2 (C, Ph), 141.7 ($\text{CH}=\text{C}$), 144.3 ($\text{CH}=\text{C}$), 171.1 (C=

N). — $C_{27}H_{45}NSn$ (502.36): calcd. C 64.56, H 9.03, N 2.79; found C 64.49, H 9.01, N 2.75.

3,3-Dimethyl-2-phenyl-5-isopropyl-3H-pyrrole (9j): 4% yield, colourless oil. — 1H NMR (200 MHz): δ = 1.26 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.40 [s, 6 H, $C(CH_3)_2$], 2.80 [septd, J = 6.7 Hz and 1.4 Hz, 1 H, $CH(CH_3)_2$], 5.74 (d, J = 1.4 Hz, 1 H, $CH=C$), 7.25–7.44 (m, 3 H, Ph), 7.90–8.00 (m, 2 H, Ph). — ^{13}C NMR (50 MHz): δ = 21.2 (CH_3), 22.9 (CH_3), 29.5 [$CH(CH_3)_2$], 55.8 [$C(CH_3)_2$], 127.8, 128.4, 128.9 and 129.7 (CH, vinyl), 133.6 (C, Ph), 159.7 (C–N), 183.0 (C=N). — $C_{15}H_{19}N$ (213.32): calcd. C 84.46, H 8.98, N 6.57; found C 84.31, H 8.97, N 6.45.

4,4-Dimethyl-2-isopropylidene-5-phenyl-3,4-dihydro-2H-pyrrole (10j): 5% yield, colourless oil. — 1H NMR (200 MHz): δ = 1.44 [s, 6 H, $C(CH_3)_2$], 1.77 (m, 3 H, CH_3), 2.12 (m, 3 H, CH_3), 2.60 (m, 2 H, CH_2), 7.36–7.40 (m, 3 H, Ph), 7.92–7.97 (m, 2 H, Ph). — ^{13}C NMR (50 MHz): δ = 19.4 (CH_3), 20.8 (CH_3), 27.7 (CH_3), 45.5 (CH_2), 48.9 [$C(CH_3)_2$], 123.1 (C=C–N), 128.3 and 129.5 (CH, Ph), 134.7 (C, Ph), 147.5 (C–N), 177.8 (C=N). — $C_{15}H_{19}N$ (213.32): calcd. C 84.46, H 8.98, N 6.57; found C 84.39, H 9.06, N 6.44.

Cyclization of **5m** gave **8m**.

6-Diethylphosphonato-2,2,5,5-tetramethyl-3-(tri-*n*-butylstannyl)-2,5-dihydropyridine (8m): 55% yield, colourless oil. — 1H NMR (400 MHz): δ = 0.84–0.91 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 1.23 [s, 6 H, $C(CH_3)_2$], 1.27–1.34 (m, 6 H, CH_2), 1.29 [s, 6 H, $C(CH_3)_2$], 1.31 (t, J = 7.2 Hz, 6 H, OCH_2CH_3), 1.41–1.48 (m, 6 H, CH_2), 4.14 (q, J = 7.2 Hz, 4 H, OCH_2CH_3), 5.45 (d, J = 9.7 Hz, 1 H, $CH=C$). — ^{13}C NMR (100 MHz): δ = 10.4 ($SnCH_2$), 13.6 ($SnCH_2CH_2CH_2CH_3$), 16.3 (CH_3), 27.3 (CH_2), 27.8 (CH_3), 29.1 (CH_2), 31.5 (CH_3), 34.9 (d, J = 29.0 Hz, C=C–N), 61.3 (d, J = 23.0 Hz, OCH_2CH_3), 62.8 (C–N), 141.8 ($CH=C$), 142.6 ($CH=C$), 168.7 (d, J = 204.2 Hz, C=N). — $C_{25}H_{50}NO_3PSn$ (514.35): calcd. C 53.40, H 8.96, N 2.49; found C 53.44, H 8.92, N 2.43.

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