NMR Studies of Five-Coordinate Tin Enolate: An Efficient Reagent for Halo Selective Reaction toward α-Halo Ketone or α-Halo Imine

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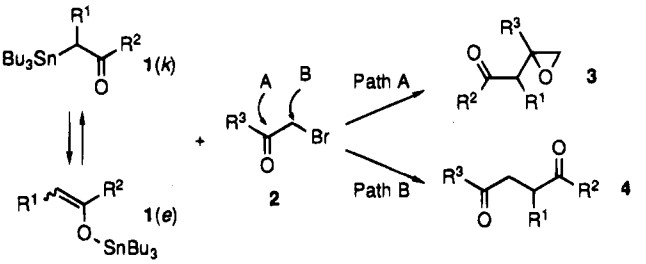
NMR studies of tin enolates **1**, in the presence of HMPA, revealed the presence of a five-coordinate *O*-stannyl enolate **1**(*h*) which contributes to upfield shifts of Sn peaks in the ^{119}Sn NMR spectrum and increased coupling constants $J(^{119}Sn-^{13}C)$, compared with the four-coordinate tin enolate **1**(*e*). The tautomeric equilibrium between *C*-stannyl ketone **1**(*k*) and *O*-stannyl enolate **1**(*e*) was changed by the addition of HMPA, the percentage of enol form being increased. The resulting five-coordinate tin enolates **1**(*h*) showed high reactivity and selectivity for halide displacement in reactions with α-halo ketones **2**. The tin enolates, when coordinated by Bu_4NBr, effected a selective reaction with α-halo imines **5** to give a variety of γ-imino ketones **6**, which were subsequently hydrolyzed to 1,4-diketones or cyclodehydrated to substituted pyrroles **9**.

Introduction

Organotin reagents have been extensively studied in the context of carbon–carbon bond formation.[1] Of particular interest are organotin enolates, which couple with electrophiles such as carbonyl compounds[2] and organic halides.[3] The α-halo ketones **2**, which have both types of electrophilic moiety, inherently react with tin enolates **1** at the carbonyl carbon. For example, the reaction of **1a** and 2-bromoacetophenone **2a** at 63 °C for 20 h was reported to give β-keto oxirane **3aa** in 79% yield (Scheme 1, Path A)[4] and was further accelerated by the addition of a Pd-catalyst.[4] Migita and co-workers have also reported that various types of tin enolates, including **1a-c**, attack α-halo ketones selectively at the carbonyl moiety, furnishing substituted furans *via* intermediate oxiranes **3**.[5]

In contrast, we have reported the reverse general chemoselectivity in the high coordination of tin enolates **1** with appropriate ligands such as HMPA, Bu_3PO, and Bu_4NBr, in which 1,4-diketones **4** were predominantly produced *via* coupling at the halide moiety of **2** (path B) under mild, nearly neutral conditions.[6] In this halo-selective reaction, we have assumed that a five-coordinate tin enolate is generated and plays a key role, but no confirming evidence has been obtained. The complete change of chemoselectivity was largely dependent on the tin enolates and the ligands employed, and in several cases, a small amount of product due to coupling at the carbonyl moiety of α-halo ketones was observed. Organotin enolates **1** usually exist as mixtures of *C*-stannyl ketone **1**(*k*) and *O*-stannyl enolate **1**(*e*), as shown in Scheme 1.

Scheme 1



a: R^1 = H, R^2 = Me
b: R^1 = H, R^2 = Ph
c: -R^1-R^2- = -$(CH_2)_4$-
d: R^1 = H, R^2 = *t*-Bu

In this paper, NMR studies of tin enolates in the presence of HMPA confirm the presence of high-coordinate *O*-stannyl enolates **1**(*h*), which may promote the reverse chemoselectivity. In addition, we describe a completely selective coupling at the halide moiety with tin enolates and α-halo imines, which are considered to be masked α-halo ketones.[7]

Results and Discussion

NMR Studies. In order to confirm the presence of high-coordinate tin enolates, three representative tin enolates **1a–c** were analyzed by ^{1}H, ^{13}C, and ^{119}Sn NMR spectrometry, under conditions similar to those of the practical synthesis of 1,4-diketones, noted in Table 2. Two

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(1) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987.

(2) (a) Noltes, J. G.; Creemers, H. M. J. C.; Van Der Kerk, G. J. M. *J. Organomet. Chem.* **1968**, *11*, 21. (b) Labadie, S. S.; Stille, J. K. *Tetrahedron* **1984**, *40*, 2329. (c) Yamamoto, Y.; Yatagi, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1981**, 162.

(3) (a) Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273. (b) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, *43*, 3791. (c) Kosugi, M.; Hagiwara, I.; Sumiya, T.; Migita, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 242. (d) Kosugi, M.; Hagiwara, I.; Migita, T. *Chem. Lett.* **1983**, 839. (e) Kosugi, M.; Koshiba, M.; Atoh, A.; Sano, H.; Migita, T. *Bull Chem. Soc. Jpn.* **1986**, *59*, 677.

(4) Pri-Bar, I.; Pearlman, P. S.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4629.

(5) Kosugi, K.; Takano, I.; Hoshino, I.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1983**, 989.

(6) (a) Baba, A.; Yasuda, M.; Yano, K.; Shibata, I.; Matsuda, H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3205. (b) Yasuda, M.; Oh-hata, T.; Shibata, I.; Baba, A.; Matsuda, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 859.

(7) De Kimpe, N.; De Cock, W.; Stevens, C. *Tetrahedron* **1992**, *48*, 2739.

0022-3263/94/1959-4386$04.50/0

Table 1. Ratios of Tin Compounds 1(*k*, *e*, and *eh*) and ^{119}Sn NMR Chemical Shifts (δ, ppm)

			1a[a]			1b[a]			1c[a]		
			k	*e*	*eh*	*k*	*e*	*eh*	*k*	*e*	*eh*
(i)[b]	without HMPA	ratio (%)	92	8		74	26		0	100	
		δ(^{119}Sn)	−3.6	92.7		1.4	104.0			91.0	
(ii)[b]	HMPA	ratio (%)	79	0	21	33	0	67	0	0	100
		δ(^{119}Sn)	−3.8		6.7	1.3		−11.0			43.5

[a] Key: *k*, keto form; *e*, enol form; *eh*, statistical average of enol form and coordinated enol form. [b] (i) Tin compound **1** in C_6D_6 (1 M). (ii) Adding 1.5 equiv of HMPA to 1 M of C_6D_6 solution of **1**.

Table 2. Reaction of Tin Enolate 1a-c with 2-Bromoacetophenone (2a)[a]

				% yield	
entry	tin enolate	ligand	condns (°C, h)	4	3
1	**1a**		80, 1	**4aa**, 0	**3aa**, 90
2	**1a**	HMPA	25, 1	**4aa**, 73	**3aa**, 12
3	**1b**		80, 4	**4ba**, 4	**3ba**, 34(27)[b]
4	**1b**	HMPA	25, 4	**4ba**, 70	**3ba**, 0(22)[c]
5	**1c**		80, 5	**4ca**, 22	**3ca**, 50
6	**1c**	HMPA	25, 1	**4ca**, 56	**3ca**, 0
7	**1c**	Bu_4NBr	25, 1.5	**4ca**, 76	**3ca**, 0

[a] All reactions were performed using tin enolate (3.6 mmol), ligand (5.4 mmol), and 2-bromoacetophenone (3.0 mmol) in dry benzene (3 mL). [b] The formation of bromohydrin derivative **3ba-1** *via* carbonyl attack was accompanied. [c] Yield of 2,4-diphenylfuran derivative by rearrangement of oxirane (Padmanabhan, S.; Ogawa, T.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2114).

types of NMR samples were prepared: (i) a 1 M solution of tin compound **1** in C_6D_6 and (ii) a 1 M C_6D_6 solution of **1** plus 1.5 equiv of HMPA. Table 1 summarizes the results of the ^{119}Sn NMR analyses. When no ligand was added, the ratios of the keto and enol forms were greatly dependent on their substituents, as shown in Table 1i. Tin enolate **1a** existed primarily in the keto form and **1c** exclusively in the enol form, in C_6D_6. Both forms were present in the case of tin enolate **1b**. Similar results have been reported by Pereyre.[8] ^{119}Sn NMR spectra of **1** showed peaks at *ca.* 0 ppm and 100 ppm, corresponding to **1**(*k*) and **1**(*e*), respectively.

Table 2 shows the results of the reaction between the tin enolates **1a−c** and 2-bromoacetophenone (**2a**). In the absence of ligands, tin enolates preferably attacked the carbonyl group of **2a** to give β-keto oxirane **3** or bromohydrin. These results precluded the idea that keto and enol forms attack the carbonyl and halide moieties, respectively, because **1c**, present as only the enol form, gave predominantly the corresponding β-keto oxirane. The chemoselectivity toward the carbonyl moiety appears to be independent of the form of the tin enolate. On the other hand, the addition of HMPA or Bu_4NBr (1.5 equiv) caused a dramatic change of chemoselectivity and produced 1,4-diketones **4** by attack at the halide carbon with all three tin enolates examined. As shown in Table1ii, NMR analyses of the tin enolates in the presence of HMPA (1.5 equiv) revealed the following features: (1) the percentage of keto form (*k*) was decreased, although no change in its chemical shift δ (^{119}Sn) was observed; (2) the signals for the enol form (*e*) disappeared, and broad signals (*eh*), corresponding to the statistical average of (*e*) and (*h*), appeared at higher field. It is reasonable to suggest that the five-coordinate tin enolate species (*h*) are also responsible for the change of chemoselectivity.

The data in Table 3, which lists ^{13}C and ^{1}H NMR chemical shifts for **1a−c**(*k*, *e*, and *eh*), suggest that **1**(*eh*) are enol forms because of the presence of signals due to vinylic carbons (C-5 and C-6) and protons (5-H). In addition, the larger coupling constants $^{1}J(^{119}Sn-^{13}C)$ (Table 4) and considerable upfield shifts in the ^{119}Sn NMR spectra relative to those of **1**(*e*) (Table 1) suggest that the species for five-coordinate *O*-stannyl enolates **1**(*h*) are present[9] and contribute to the equilibrium. As a consequence, HMPA would coordinate not to *C*-stannyl ketones **1**(*k*), but exclusively to *O*-stannyl enolates **1**(*e*), to lead to the decrease in the percentage of keto form **1**(*k*) as shown in Scheme 2.

The resulting five-coordinate *O*-stannyl enolates **1**(*h*) effected the selective formation of 1,4-diketones. Moreover, the reactivity was considerably enhanced by the coordination. The enolate **1**(*h*) underwent the addition even at room temperature, in contrast to **1**(*e*) for which heating was required (Table 2, entries 1, 3, and 5). The larger difference of δ (^{13}C) between C-5 and C-6 in **1**(*eh*) relative to that in **1**(*e*) indicates a higher degree of polarization at the reaction site in **1**(*h*), leading to the facile coupling reaction under mild conditions.

Increasing the amount of HMPA led to an increase in both the percentage of enol form and the degree of hypervalency of the tin center, as depicted in Figures 1 and 2, respectively.[9] The ratio of the $^{1}J(^{119}Sn-^{13}C)$ value (470.6 Hz) of **1a** with 5.0 equiv of HMPA to that of **1a** (362.2 Hz) without HMPA is 1.30, which is close to the theoretical ratio of 1.33[9b] for five-coordinate to four-coordinate tin. Accordingly, the equilibrium between *e* and *h* lies well toward the five-coordinate tin enolate *h*, when 5 equiv of HMPA is present. As already reported, 5 equiv of HMPA gave 1,4-diketone **4aa** exclusively, from **1a** and **2a**,[6] and this is consistent with our suggestion that five-coordinate tin enolate **1**(*h*) is responsible for the change of chemoselectivity. The best yield of 1,4-diketone **4aa**, however, was obtained in the presence of 1.5 equiv of HMPA.[6] The degree of hypervalency increased only slightly in the presence of greater than 1 equiv of HMPA, as shown in Figure 2. Excess "free" HMPA might even prevent the interaction of five-coordinate tin enolate with **2a**.

(8) Pereyre, M; Bellegarde, B; Mendelsohn, J; Valade, J. *J. Organomet. Chem.* **1968**, *11*, 97.

(9) In general, an increase of coordination number of tin compounds from four to five causes an upfield shift of δ (^{119}Sn) and high values of coupling constants $^{n}J(^{119}Sn-^{13}C)$. For example, see: (a) Holecek, J.; Nadvornik, M.; Handlir, K. *J. Organomet. Chem.* **1983**, *241*, 177. (b) Nadvornik, M.; Holecek, J.; Handlir, K. *J. Organomet. Chem.* **1984**, *275*, 43.

(10) The generation of the naked enolate anion also may be considered in terms of the following equation, which proposes its formation by attack of fluoride ion at silicon in silyl enolate. For example, see: (a) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932. (b) Chuit, C.; Corriu, R. J. P.; Reyé, C. *J. Organomet. Chem.* **1988**, *358*, 57. In our NMR examination of the mixture of tin enolate **1a-c** and Bu_4NBr, however, the signals for neither Bu_3SnBr nor its complex with Bu_4NBr, $[Bu_3SnBr_2]^-$ Bu_4N^+, were observed.

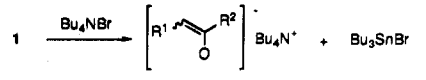
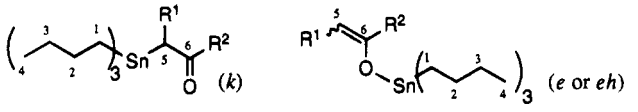


Table 3. ^{13}C and ^{1}H NMR Chemical Shifts (δ, ppm) of Tin Compounds 1



	1a			1b			1c		
position	*k*	*e*	*eh*	*k*	*e*	*eh*	*k*	*e*	*eh*
^{13}C NMR									
C-1	10.4	15.6	17.7	10.8	15.9	18.4	–	15.6	16.9
C-2	29.2	28.2	28.6	29.1	28.2	28.7	–	28.3	28.5
C-3	27.5	27.4	27.6	27.5	27.4	27.7	–	27.4	27.5
C-4	13.8	*a*	14.0	13.8	*a*	14.0	–	13.9	13.9
C-5	29.6	84.0	81.8	25.4	84.9	82.1	–	96.7	95.6
C-6	204.4	163.5	164.2	198.1	162.6	163.4	–	157.4	157.8
others		*Me*C=O			aroma			ring	
	30.3	24.1	25.0	138.9	140.7	142.8	–	24.9	25.1
				132.0	128.1	127.7		24.6	24.4
				128.5	127.8	126.9		23.6	23.8
				128.2	126.0	126.1			
^{1}H NMR[b]									
5-H	2.17 (s)	3.92 (s)	3.83 (s)	2.77 (s)	4.74 (d, 1.1)	4.65 (s)	–	4.59 (t, 3.7)	4.60 (t, 3.7)
		3.78 (s)	3.77 (s)		4.13 (d, 1.1)	4.12 (s)	–		
others		*Me*C=O			aroma			ring	
	2.00 (s)	2.07 (s)	2.07 (s)		8.1–7.8[c] (m)	8.2–7.9[d] (m)	–	2.3 (m)	2.32 (m)
					7.4–7.1[c] (m)	7.4–7.2[d] (m)	–	1.9–1.5 (m)	1.9–1.5 (m)

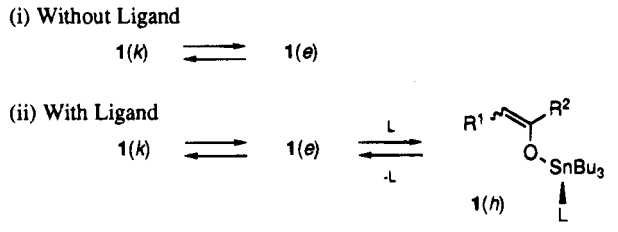
[a] Obscured by other signals. [b] Multiplicity and coupling constant in parentheses. [c] Mixture of **1b**(*k*) and **1b**(*e*). [d] Mixture of **1b**(*k*) and **1b**(*eh*).

Table 4. $^{119}Sn-^{13}C$ Coupling Constants ($^{n}J_{SnC}$, Hz) of Tin Compounds 1

	1a			1b			1c		
	k	*e*	*eh*	*k*	*e*	*eh*	*k*	*e*	*eh*
$^{1}J_{SnC}$	330.9	362.2	445.8	330.0	359.4	464.2	360.3	409.1	
$^{2}J_{SnC}$	21.1	*a*	25.7	21.1	21.1	*a*	21.1	22.1	
$^{3}J_{SnC}$	57.9	*a*	*a*	57.0	58.8	*a*	64.4	67.1	

[a] Obscured by other signals.

Scheme 2



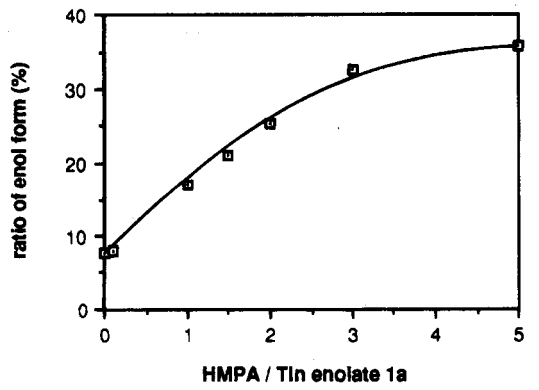


Figure 1. Correlation of the ratio of enol form with equivalents of HMPA to tin enolate **1a**.

On the other hand, an attempt to confirm the presence of Bu_4NBr-coordinated enolates was unsuccessful. In NMR studies, signals corresponding to *C*-stannyl derivatives were absent, and no signals for *O*-stannyl species were detected either,[11] perhaps due to an instability of the resulting coordinated enolates. A considerably higher yield of 1,4-diketone **4ca**, in fact, was obtained with Bu_4NBr (entry 7 in Table 2). In the next section, another application of Bu_4NBr to this general system is discussed.

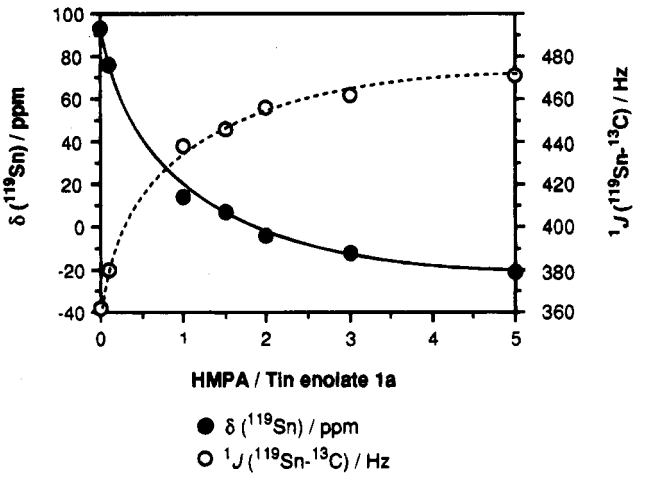


Figure 2. Correlation of chemical shift δ (^{119}Sn) and coupling constant ^{1}J ($^{119}Sn-^{13}C$) with equivalents of HMPA to tin enolate **1a**.

Reaction of Five-Coordinate Organotin Enolates with α-Halo Imines. In the synthesis of 1,4-diketones from high-coordinate tin enolates and α-bromo ketones, the formation of oxiranes could not be completely suppressed in many cases. In order to overcome this complication, we attempted the coupling with α-halo imines **5** instead of α-halo ketones. The α-halo imines are readily available from the corresponding α-halo carbonyl compounds.[7,11] We anticipated that the lower reactivity of imino moieties relative to carbonyl groups might lead to a selective coupling at the halide moieties of **5** (Scheme 3).

(11) De Kimpe, N.; Verhe, R.; De Buyck, L.; Moens, L.; Schamp, N. *Synthesis* **1982**, 43.

Scheme 3

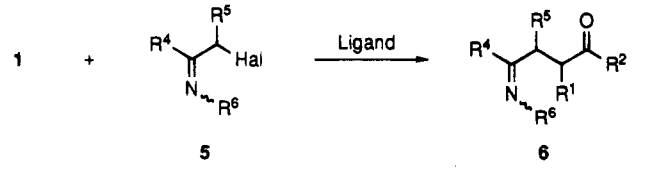


Table 5. Effect of Ligands and Solvents in the Reaction of Tin Enolate 1a and α-Bromo Imine 5a[a]

entry	solvent	ligand	ligand/1a	T, °C	time, h	% yield of 6aa
1	THF			63	45	0
2	THF	Bu_4NBr	0.1	63	21	16
3	THF	Bu_4NBr	1.0	25	1	69
4	THF	Bu_4NBr	1.5	25	2.5	80
5	THF	Bu_4NBr	2.5	25	4	59
6	THF	Et_4NBr	1.5	63	17.5	2
7	THF	Me_4NBr	1.5	63	17.5	0
8	THF	HMPA	1.5	63	3.5	66
9	THF	Bu_3PO	1.5	63	23	47
10	C_6H_6	Bu_4NBr	1.5	25	8	60
11	C_6H_6	Bu_4NBr	1.5	80	1	79
12	CH_3CN	Bu_4NBr	1.5	25	8	41
13	$(CH_2Cl)_2$	Bu_4NBr	1.5	25	22.5	25

[a] Reaction conditions: tin enolate **1a** (3.6 mmol), α-bromo imine **5a** (3.0 mmol), ligand (0–2.5 equiv), solvent (3 mL).

Employing **1a** and **5a** (R^4 = *t*-Bu, R^5 = H, R^6 = *i*-Pr), various reaction conditions were examined, as shown in Table 5. Although HMPA and Bu_3PO had an impact on the reaction only at elevated temperature (entries 8 and 9), Bu_4NBr efficiently promoted the selective synthesis of γ-imino ketone **6aa** even at room temperature (entry 4). Neither Et_4NBr nor Me_4NBr showed activity, even in refluxing THF, because of their low solubility. Most effective was 1.5 equiv of Bu_4NBr in THF.

Table 6 summarizes the synthesis of γ-imino ketones **6** from various types of tin enolates **1a-d** and α-halo imines **5a-g**. α-Halo imines proved to be less active than the parent α-halo ketones as exemplified by the observation that bromopinacolone, the parent ketone of **5a**, was readily activated, even by HMPA, to couple with **1a** in 79% yield,[6] while **5a** was activated only by Bu_4NBr. In no case were products due to attack on an imino carbon detected. The synthetic potential of the efficient coupling of α-chloro imines **5d** and **5e** or α-bromo aldimine **5g** is noteworthy, since the coupling reaction with both parent α-halo carbonyls took place only at their carbonyl moieties, furnishing chlorohydrins[4] or oxiranes,[6] respectively.

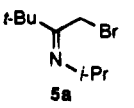
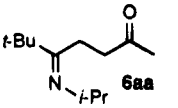
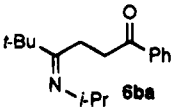
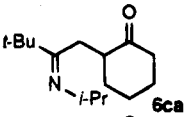
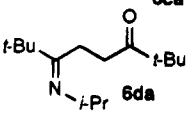
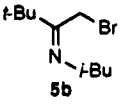
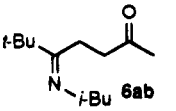
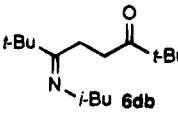
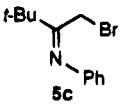
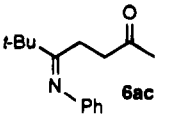
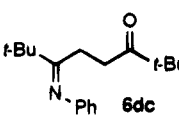
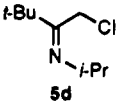
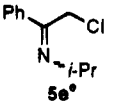
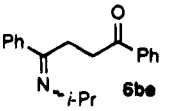
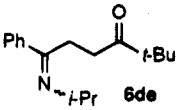
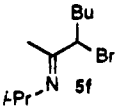
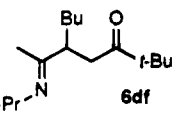
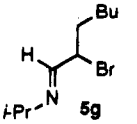
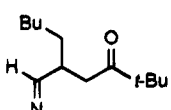
Scheme 4 illustrates the transformation of 2-chloroacetophenone (**7**) to 1,4-diketone **4aa** (49% yield based on **7**) *via* hydrolysis of the imino ketone **6ae**, which was confirmed by ^1H NMR spectroscopy.[12] An attempt to directly synthesize **4aa** from **1a** and **7** was unsuccessful and led to the exclusive formation of **8**. Similarly, 1,4-diketone **4da** (R^1 = H, R^2 = *t*-Bu, R^3 = Ph) was isolated in 45% yield after direct silica gel chromatography of the reaction mixture of **1d** and **5e**.

It was found that some product imino ketones gradually converted to substituted pyrroles, which were formed by intramolecular attack of nitrogen on the carbonyl carbon and subsequent dehydration.

For example, **6ca** was converted to pyrrole **9ca** (43%), along with 1,4-diketone **10** (55%), upon standing at room temperature for 24 h (Scheme 5). Imino ketones bearing

(12) γ-Imino ketone **6ae** could not be isolated, and the crude reaction mixture included two regioisomers (6:4) which showed the following: ^1H NMR (90 MHz, $CDCl_3$) 3.87 (septet, J = 6.3 Hz, NH), 3.1–2.5 (m, CH_2CH_2), 2.10 (s, *Me*CO), 1.22 (d, J = 6.3 Hz, $CHMe_2$) and 3.39 (septet, J = 6.3 Hz, NH), 2.73 (s, CH_2CH_2), 2.19 (s, *Me*CO), 1.00 (d, J = 6.3 Hz, $CHMe_2$).

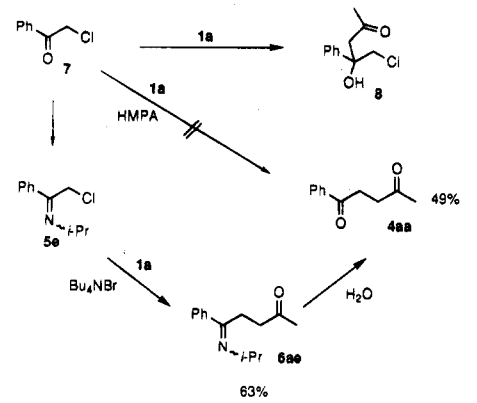
Table 6. Synthesis of γ-Imino Ketone 6 from Tin Enolate 1 and α-Halo Imine 5[a]

entry	tin enolate	α-halo imine	time, h	product	% yield
1	1a	 5a	2.5	 6aa	80
2	1b		2.5	 6ba	52[b]
			1		63[c]
3	1c		16	 6ca	98
4	1d		17	 6da	90
5	1a	 5b	8	 6ab	43
6	1d		22	 6db	77
7	1a	 5c	8	 6ac	41
8	1d		7	 6dc	92
9	1a	 5d	4	6aa	52
10	1b		1	6ba	40[b]
11	1c		2	6ca	72[b]
12	1d		20	6da	53
13	1b[d]	 5e[e]	2	 6be	51[f]
14	1d		2	 6de	65[b,g]
15	1d[d]	 5f	8	 6df	54[b]
16	1d[d]	 5g	8	 6dg	57[c]

[a] Reaction conditions: tin enolate **1** (3.6 mmol), α-halo imine **5** (3.0 mmol), Bu_4NBr (5.4 mmol), solvent THF (3 mL), 25 °C. [b] 63 °C. [c] Solvent benzene (3 mL), 80 °C. [d] Tin enolate **1** (6.0 mmol), Bu_4NBr (9.0 mmol). [e] *E*/*Z* = 1/1. [f] *E*/*Z* = 4/7. [g] *E*/*Z* = 3/2.

tert-butyl groups at their carbonyl carbons are not transformed into pyrroles. On the other hand, when the substituent R^6 has *syn* orientation to R^4, as in the case of α-halo imine **5f** and **5g**, the cyclization to a pyrrole

Scheme 4



Scheme 5

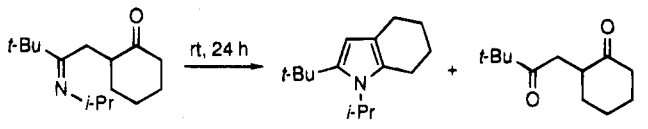
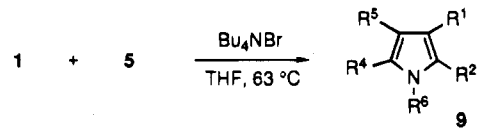


Table 7. Synthesis of Pyrrole 9 from Tin Enolate 1 and α-Bromo Imine 5[a]



		α-bromo imine					pyrrole	
entry	tin enolate		R^4	R^5	R^6	time, h		yield, %
1	**1a**	**5f**	Me	*n*-Bu	*i*-Pr	6	**9af**	32
2	**1a**	**5g**	H	*n*-pentyl	*i*-Pr	24	**9ag**	45
3	**1b**	**5g**	H	*n*-pentyl	*i*-Pr	69	**9bg**	31
4	**1c**	**5g**	H	*n*-pentyl	*i*-Pr	2	**9cg**	43

[a] Reaction conditions: tin enolate **1** (3.6 mmol), α-bromo imine **5** (3.0 mmol), Bu_4NBr (5.4 mmol), THF (3 mL), 63 °C.

was observed. Thus, the degree of steric congestion around the imino nitrogen dictates the outcome. Using these *syn*-halo imines, direct syntheses of substituted pyrroles **9** were attained as shown in Table 7.

The Paar–Knorr procedure gives substituted pyrroles from 1,4-diketones with amines under vigorous conditions.[13] Wittig has also reported the direct formation of pyrroles *via* the addition of lithium *N*-vinylamide to α-halo imines at −78 °C.[14] Our high-coordination method provides alternative, convenient access to pyrroles under much milder conditions.

Experimental Section

General. Melting points were taken on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded as thin films or as solids in KBr pellets on a Hitachi 260-30 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with a Hitachi R-90H (90 and 22.6 MHz) or a JEOL JNM-GSX-400 (400 and 100 MHz) spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303 or a Shimadzu GCMS-QP2000A spectrometer. GLC analyses were performed on a Shimadzu GC-8A with FID using a 2-m × 3 -mm column packed with SE-52. Flash chromatography was performed on silica gel (Wakogel C-300). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^1H NMR using internal standards.

Materials. THF and benzene were distilled from sodium and benzophenone. HMPA was distilled from CaH_2. Tin enolates **1a-d** were prepared by known methods.[8]

2-Bromoacetophenone (**2a**), 1-bromopinacolone, 1-chloropinacolone, and 2-chloroacetophenone were commercial products. 3-Bromoheptan-2-one[15] and 2-bromoheptanal[16] were prepared according to described methods. α-Halo imines **5a**, **5d**, and **5e** were prepared by condensation of the corresponding α-halo ketones with isopropylamine.[7] Other α-halo imines **5b**, **5f**, and **5g** were also prepared in accordance with the described methods.[7] α-Halo imines **5** were unstable and used immediately for further reaction.

Preparation and Measurement of NMR Samples. The samples (i) were prepared from tin enolates **1** (0.4 mmol) in C_6D_6 (0.4 mL) and the samples (ii) from tin enolates **1** (0.4 mmol) and HMPA (0.6 mmol) in C_6D_6 (0.4 mL). Values are given in δ. ^{119}Sn NMR spectra were recorded at room temperature on a JEOL JNM-GSX-400 (149 MHz) with Me_4Sn as internal standard.

General Procedure for Synthesis of 1,4-Diketones (4) and β-Keto Oxiranes (3). These synthetic methods and the spectral data of compounds **4aa**, **4ba**, **4ca**, and **3aa** were described in our previous paper[6] and **4da** in the literature.[17]

2-Phenacyl-2-phenyloxirane (3ba). Obtained from **1b** and **2a** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 5:1): IR (neat) 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.0–7.2 (m, 10H), 3.78 (dd, 1H, J = 16.61, 0.98 Hz), 3.59 (d, 1H, J = 16.61 Hz), 3.12 (d, 1H, J = 4.89 Hz), 2.98 (dd, 1H, J = 4.89, 0.98 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 195.9, 139.4, 136.4, 132.9, 128.2, 127.94, 127.87, 127.3, 125.4, 56.7, 54.9, 44.9; MS *m/z* 238 (M^+); HRMS calcd for $C_{16}H_{14}O_2$ 238.0994, found *m/z* 238.0979 (M^+).

2-(2-Oxocyclohexyl)-2-phenyloxirane (3ca). Obtained from **1c** and **2a** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 5:1): IR (neat) 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.46–7.22 (m, 5H), 2.97 (d, 1H, J = 4.88 Hz), 2.89 (d, 1H, J = 4.88 Hz), 2.51–1.41 (m, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 209.5, 138.2, 128.9, 127.5, 127.4, 59.4, 58.7, 54.8, 42.1, 29.6, 26.5, 24.5; MS *m/z* 216 (M^+). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.45; H, 7.46. Found: C, 77.51; H, 7.62.

2-(3,3-Dimethyl-2-oxobutyl)cyclohexanone (10): ^1H NMR (400 MHz, $CDCl_3$) 3.05 (dd, 1H, J = 17.58, 6.83 Hz), 2.98 (m, 1H), 2.38 (t, 2H, J = 4.88 Hz), 2.23 (dd, 1H, J = 17.58, 4.89 Hz), 2.17–2.03 (m, 2H), 1.87–1.59 (m, 3H), 1.41–1.21 (m, 1H), 1.17 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 214.1, 211.4, 46.1, 44.1, 41.9, 36.6, 34.1, 28.0, 26.5, 25.4; HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found *m/z* 196.1435 (M^+).

4-Bromo-3-hydroxy-1,3-diphenylbutan-1-one (3ba-1). A mixture of tin enolate **1b** (2.04 g, 5.0 mmol) and 2-bromoacetophenone (**2a**) (0.80g, 4.0 mmol) in dry THF (4 mL) was stirred at room temperature under nitrogen for 5 h. This reaction mixture was added to diethyl ether (100 mL) and aqueous NH_4F (15%; 40 mL), stirred for 1 h, and washed with water (50 mL × 2), dried ($MgSO_4$), and evaporated. The residue was flash chromatographed, and title compound **3ba-1** (eluted by hexane–diethyl ether, 5:1) was isolated as an oil in 42% yield: IR (neat) 3450, 1670 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 8.0–7.0 (m, 10H), 4.98 (s, 1H), 3.94 (d, 1H, J = 17.36 Hz), 3.70 (s, 2H), 3.66 (d, 1H, J = 17.36 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 200.2, 143.1, 136.7, 133.5, 128.4, 128.2, 127.9, 127.4, 125.0, 74.7, 45.2 (t, $^1J_{CH}$ = 126.8 Hz, C-2), 42.8 (t, $^1J_{CH}$ = 152.7 Hz, C-4). Satisfactory high resolution mass spectral and elemental analysis data for the title compound **3ba-1** could not be obtained due to its instability. IR and ^1H and ^{13}C NMR data were in good analogy[6] with those of 4-chloro-3-hydroxy-1,3-diphenylbutan-1-one or 5-bromo-4-hydroxy-4-phenylpentan-2-one.

(13) (a) Paal, C. *Chem. Ber.* **1884**, *17*, 2756. (b) Knorr, L. *Chem. Ber.* **1884**, *17*, 2863.
(14) Wittig, G.; Roderer, R.; Fischer, S. *Tetrahedron Lett.* **1973**, 3517.
(15) Bedoukian, P. Z. *J. Am. Chem. Soc.* **1945**, *67*, 1430.
(16) Duhamel, P.; Duhamel, L.; Valnot, J.-Y. *Bull. Soc. Chim. Fr.* **1973**, 1465.
(17) Russell, G. A.; Kulkarni, S. V.; Khanna, R. K. *J. Org. Chem.* **1990**, *55*, 1080.

***N*-(1-Bromo-3,3-dimethyl-2-butylidene)isobutylamine (5b).** To a mixture of 1-bromopinacolone (50 mmol) and $TiCl_4$ (30 mmol) in 80 mL of diethyl ether was added dropwise a solution of isobutylamine (200 mmol) in 20 mL of diethyl ether at 0 °C, the mixture was stirred for 3 h at room temperature, and 0.5 N NaOH (100 mL) was added to the reaction mixture. It was then filtered, and the water layer was extracted with diethyl ether. After the mixture was dried over $MgSO_4$ and solvent was evaporated, the crude product was purified by distillation at reduced pressure (63% yield): bp 64 °C/2 mmHg; IR (neat) 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.78 (s, 2H), 3.21 (d, 2H, J = 6.84 Hz), 2.02–1.92 (m, 1H), 1.19 (s, 9H), 0.94 (d, 6H, J = 6.84 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 169.6, 58.7, 40.8, 29.8, 28.3, 20.6, 17.2; MS *m/z* 235 (M^+ + 2), 233 (M^+); HRMS calcd for $C_{10}H_{20}NBr$ 233.0779, found *m/z* 233.0774 (M^+).

***N*-(1-Bromo-3,3-dimethyl-2-butylidene)aniline (5c).** The preparation of **5c** was analogous to that described for the synthesis of **5b**. The title compound was obtained from 1-bromopinacolone (50 mmol) and aniline (200 mmol) in the presence of $TiCl_4$ (30 mmol) in 46% yield: bp 74 °C/2 mmHg; IR (neat) 1600 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 7.6–6.6 (m, 5H), 3.77 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 173.3, 150.0, 128.6, 123.1, 118.3, 40.0, 28.8, 18.8; MS *m/z* 253 (M^+), 251 (M^+ − 2); HRMS calcd for $C_{12}H_{16}NBr$ 253.0466, found *m/z* 253.0465 (M^+).

***N*-(3-Bromo-2-heptylidene)isopropylamine (5f).** The preparation of **5f** was analogous to that described for the synthesis of **5b**. The title compound was obtained from 3-bromoheptan-2-one (50 mmol) and isopropylamine (200 mmol) in the presence of $TiCl_4$ (30 mmol) in 80% yield: bp 42 °C/1 mmHg; IR (neat) 1660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 4.43 (t, 1H, J = 7.81 Hz), 3.64 (septet, 1H, J = 6.35 Hz), 1.94 (s, 3H), 1.5–1.2 (m, 6H), 1.12 (d, 1H, J = 6.35 Hz), 1.10 (d, 1H, J = 6.35 Hz), 0.90 (t, 3H, J = 6.84 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 163.6, 60.6, 50.6, 35.5, 29.8, 22.0, 23.0, 22.8, 13.7; MS *m/z* 236 (M^+ + 3), 234 (M^+ + 1); HRMS calcd for $C_{10}H_{20}NBr$ 233.0779, found *m/z* 234.0878 (M^+ + 1).

***N*-(2-Bromo-1-heptylidene)isopropylamine (5g).** The preparation of **5g** was analogous to that described for the synthesis of **5b**. The title compound was obtained from 2-bromoheptanal (50 mmol) and isopropylamine (200 mmol) in the presence of $TiCl_4$ (30 mmol) in 55% yield: bp 54 °C/2 mmHg; IR (neat) 1660 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 7.59 (d, 1H, J = 7.04 Hz), 4.41 (dt, 1H, J = 7.04, 7.03 Hz), 3.37 (septet, 1H, J = 6.37 Hz), 2.2–0.7 (m, 11H), 1.16 (d, 6H, J = 6.37 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 159.2, 60.3, 54.0, 35.6, 31.0, 26.9, 23.8 and 23.5 (2 × NCH*Me*), 22.3, 13.8; MS *m/z* 235 (M^+ + 2), 233 (M^+); HRMS calcd for $C_{10}H_{20}NBr$ 233.0779, found *m/z* 233.0797 (M^+).

General Procedure for Synthesis of γ-Imino Ketones (6). A mixture of a tin enolate (3.6 mmol) and an additive (5.4 mmol) in dry solvent (3 mL) was stirred for 10 min under nitrogen. To this solution was added an α-halo imine (3.0 mmol), and stirring continued under the reaction conditions noted in Table 6. Volatiles were removed under reduced pressure, and solids precipitated on addition of hexane. The hexane layer was then pipeted out. The treatment was repeated a few times, and the collected hexane solution was evaporated. Kugelrohr distillation gave the γ-imino ketone **6**. The configurations of **6** were assigned as follows. α-Halo imines **5a–d** (R^4 = *t*-Bu) having the *Z*-form (*t*-Bu and R^6 are in the *anti*-configuration) were prepared in accordance with the described methods[7] coupled with **1** at halide moiety to form (*E*)-γ-imino ketones **6aa**, **6ba**, **6ca**, **6da**, **6ab**, **6db**, **6ac,** and **6dc** (*t*-Bu and R^6 are in the *anti*-configuration). All these *anti* isomers showed ^{13}C NMR chemical shifts ($^{13}CH_2C{=}N$) at *ca.* 21–25 ppm. There are considerable differences in the chemical shifts ($^{13}CH_2C{=}N$) of two isomers of **6be** and **6de**, respectively, which are *ca.* 22 ppm and 35 ppm. Thus, the formers were identified to be *E*-isomers (Ph and *i*-Pr are in the *anti*-configuration) and the latters were *Z*-isomers (*syn*) by comparison with the data of **6** bearing *t*-Bu at R^4 (*anti*). **5f** and **5g**, and their products (**6df** and **6dg**) could be determined to have the *E*-form because of sterical hindrance.[7]

***N*-(6,6-Dimethyl-2-oxo-5-heptylidene)isopropylamine (6aa).** Obtained from **1a** and **5a** according to the general procedure by distillation: bp 60 °C/2 mmHg; IR (neat) 1730, 1660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.54 (septet, 1H, J = 6.34 Hz), 2.54–2.44 (m, 4H), 2.16 (s, 3H), 1.08 (s, 9H), 1.06 (d, 6H, J = 6.34 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 206.5, 172.1, 49.8, 42.0, 40.4, 29.8, 28.1, 23.9, 20.7; MS *m/z* 197 (M^+), 140 ($M^+ - C_4H_9$); HRMS calcd for $C_{12}H_{23}NO$ 197.1780, found *m/z* 197.1775 (M^+). Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.01. Found: C, 72.66; H, 11.74; N, 6.67.

***N*-(5,5-Dimethyl-1-oxo-1-phenyl-4-hexylidene)isopropylamine (6ba).** Obtained from **1b** and **5a** according to the general procedure by distillation to afford **6ba** as solid: bp 90 °C/0.07 mmHg; mp 70.5 °C (from hexane); IR (neat) 1680, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.94 (m, 2H), 7.4–7.6 (m, 3H), 3.63 (septet, 1H, J = 6.35 Hz), 3.08–3.04 (m, 2H), 2.67–2.63 (m, 2H), 1.13 (s, 9H), 1.10 (d, 6H, J = 6.35 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 198.1, 172.3, 136.1, 133.1, 128.5, 127.8, 49.9, 40.4, 37.0, 28.1, 24.0, 21.0; MS *m/z* 259 (M^+), 202 ($M^+ - C_4H_9$). Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.84; H, 9.78; N, 5.42.

[3,3-Dimethyl-1-(2-oxocyclohexyl)-2-butylidene]isopropylamine (6ca). Obtained from **1c** and **5a** according to the general procedure by distillation: bp 100 °C/2 mmHg; IR (neat) 1700, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.57 (septet, 1H, J = 6.10 Hz), 2.70 (dd, 1H, J = 13.91, 3.90 Hz), 2.36 (dd, 1H, J = 13.91, 10.01 Hz), 1.08 (s, 9H), 0.99 (d, 6H, J = 6.10 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 211.5, 171.9, 50.0, 49.5, 42.2, 40.2, 33.9, 28.9, 27.9, 25.63, 25.58, 24.0 and 23.9 (2 × NCH*Me*). Satisfactory high-resolution mass spectral and elemental analysis data for the title compound **6ca** could not be obtained due to its rapid cyclization to pyrrole **9ca**.

***N*-(2,2,7,7-Tetramethyl-3-oxo-6-octylidene)isopropylamine (6da).** Obtained from **1d** and **5a** according to the general procedure by distillation: bp 90 °C/0.1 mmHg; IR (neat) 1710, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.53 (septet, 1H, J = 6.35 Hz), 2.57–2.51 (m, 2H), 2.47–2.41 (m, 2H), 1.15 (s, 9H), 1.08 (s, 9H), 1.07 (d, 6H, J = 6.35 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 213.6, 172.4, 49.6, 43.8, 40.1, 34.9, 27.9, 26.3, 23.8, 21.0; MS *m/z* 239 (M^+), 182 ($M^+ - C_4H_9$); HRMS calcd for $C_{15}H_{29}NO$ 239.2249, found *m/z* 239.2253 (M^+). Anal. Calcd for $C_{15}H_{29}NO$: C, 75.26; H, 12.21; N, 5.85. Found: C, 75.64; H, 11.83; N, 5.89.

***N*-(6,6-Dimethyl-2-oxo-5-heptylidene)isobutylamine (6ab).** Obtained from **1a** and **5b** according to the general procedure by distillation: bp 85 °C/1 mmHg; IR (neat) 1720, 1640 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.06 (d, 2H, J = 6.37 Hz), 2.51 (s, 4H), 2.16 (s, 3H), 1.6–2.1 (m, 1H), 1.10 (s, 9H), 0.90 (d, 6H, J = 6.59 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) 206.8, 175.6, 58.5, 40.9, 40.6, 30.0, 29.7, 27.9, 20.9, 20.5; MS *m/z* 211 (M^+), 154 ($M^+ - C_4H_9$); HRMS calcd for $C_{13}H_{25}NO$ 211.1936, found *m/z* 211.1926 (M^+).

***N*-(2,2,7,7-Tetramethyl-3-oxo-6-octylidene)isobutylamine (6db).** Obtained from **1d** and **5b** according to the general procedure by distillation: bp 60 °C/0.05 mmHg; IR (neat) 1710, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.06 (d, 2H, J = 6.84 Hz), 2.57–2.45 (m, 4H), 2.01–1.80 (m, 1H), 1.15 (s, 9H), 1.10 (s, 9H), 0.90 (d, 6H, J = 6.84 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 213.9, 176.1, 58.5, 44.1, 40.9, 33.7, 30.1, 27.9, 26.4, 21.5, 20.6; MS *m/z* 253 (M^+), 196 ($M^+ - C_4H_9$); HRMS calcd for $C_{16}H_{31}NO$ 253.2406, found *m/z* 253.2409 (M^+). Anal. Calcd for $C_{16}H_{31}NO$: C, 75.83; H, 12.33; N, 5.53. Found: C, 75.51; H, 12.05; N, 5.14.

***N*-(6,6-Dimethyl-2-oxo-5-heptylidene)aniline (6ac).** Obtained from **1a** and **5c** according to the general procedure by distillation: bp 120 °C/1 mmHg; IR (neat) 1720, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.43–6.68 (m, 5H), 2.80–2.77 (m, 2H), 2.70–2.67 (m, 2H), 2.20 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 205.8, 178.9, 151.1, 128.8, 122.4, 118.3, 40.9, 40.7, 29.2, 27.8, 22.4; MS *m/z* 231 (M^+), 174 ($M^+ - C_4H_9$); HRMS calcd for $C_{15}H_{21}NO$ 231.1623, found *m/z* 231.1642 (M^+).

***N*-(2,2,7,7-Tetramethyl-3-oxo-6-octylidene)aniline (6dc).** Obtained from **1d** and **5c** according to the general procedure by distillation: bp 120 °C/0.1 mmHg; IR (neat) 1710, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.19 (m, 2H), 6.89 (m, 1H), 6.59 (m, 2H), 2.46–2.29 (m, 4H), 1.16 (s, 9H), 0.85 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 213.5, 179.5, 151.3, 128.8, 122.4, 118.5, 43.8, 41.0, 33.7, 27.8, 26.1, 23.1; MS *m/z* 273 (M^+), 216 ($M^+ - C_4H_9$); HRMS calcd for $C_{18}H_{27}NO$ 273.2093, found *m/z*

273.2071 (M^+). Anal. Calcd for $C_{18}H_{27}NO$: C, 79.07; H, 9.95; N, 5.12. Found: C, 78.98; H, 9.62; N, 5.21.

***N*-(1,4-Diphenyl-1-oxo-4-butylidene)isopropylamine (6be).** Obtained from **1b** and **5e** according to the general procedure by distillation. It was isolated as a mixture of (*E*)- and (*Z*)-**6be** (*E*/*Z* = 4/7): bp 150 °C/0.1 mmHg; mp 87–90 °C (from hexane); IR (KBr) 1680, 1650 cm^{-1}; MS *m/z* 279 (M^+), 222 ($M^+ - C_4H_9$); HRMS calcd for $C_{19}H_{21}NO$ 279.1623, found *m/z* 279.1611 (M^+); ^1H NMR (400 MHz, $CDCl_3$) 8.06–7.15 (aroma, *E* and *Z*), (*E*)-**6be** 3.23 (septet, 1H, *J* = 6.35 Hz), 3.13–3.09 (m, 4H), 1.24 (d, 6H, *J* = 6.35 Hz), (*Z*)-**6be** 3.43 (septet, 1H, *J* = 6.10 Hz), 3.29 (t, 2H, *J* = 6.93 Hz), 2.93 (t, 2H, *J* = 6.93 Hz), 0.95 (d, 6H, 6.10 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 199.5 (s, C-1, *E* and *Z*), 166.1 and 164.5 (s, C-4, *Z* and *E*), 139.3, 137.6, 132.9, 132.3, 129.1, 128.4, 128.2, 127.9, 127.8, 127.7, 126.9, 126.0 (aroma), 51.7 and 51.0 (d, NC, *Z* and *E*), 36.1 and 34.4 (t, C-2, *E* and *Z*), 35.7 and 22.7 (t, C-3, *Z* and *E*), 24.0 and 23.8 (q, CH*Me*$_2$, *E* and *Z*). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.55; H, 7.55; N, 4.91. Further recrystallizing from hexane gave single isomer (*Z*)-**6be** as white crystals: mp 87.5 °C; ^1H NMR (400 MHz, $CDCl_3$) 8.06–7.15 (m, 10H), 3.41 (septet, 1H, *J* = 6.11 Hz), 3.30 (t, 2H, *J* = 6.93 Hz), 2.93 (t, 2H, *J* = 6.93 Hz), 0.96 (d, 6H, *J* = 6.11 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 199.9, 166.6, 139.3, 137.6, 132.6, 128.4, 128.1, 127.9, 126.1, 51.9, 35.7, 34.5, 23.8.

***N*-(2,2-Dimethyl-3-oxo-6-phenyl-6-hexylidene)isopropylamine (6de).** Obtained from **1d** and **5e** according to the general procedure by distillation. It was isolated as a mixture of (*E*)- and (*Z*)-**6de** (*E*/*Z* =3/2): bp 110 °C/0.1 mmHg; IR (neat) 1710, 1650 cm^{-1}; MS *m/z* 259 (M^+), 202 ($M^+ - C_4H_9$); HRMS caled for $C_{17}H_{25}NO$ 259.1936, found *m/z* 259.1915 (M^+); ^1H NMR (400 MHz, $CDCl_3$) 8.01–7.13 (aroma, *E* and *Z*), (*E*)-**6de** 3.39 (septet, 1H, *J* = 6.35 Hz), 2.84 (t, 2H, *J* = 6.59 Hz), 2.70 (t, 2H, *J* = 6.59 Hz), 1.23 (d, 6H, *J* = 6.35 Hz), 1.17 (s, 9H), (*Z*)-**6de** 3.12 (septet, 1H, *J* = 6.35 Hz), 2.94 (t, 2H, *J* = 7.82 Hz), 2.59 (t, 2H, *J* = 7.82 Hz), 1.09 (d, 6H, *J* = 6.35 Hz), 1.07 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 214.7 (s, C-3, *E* and *Z*), 166.7 and 165.1 (s, C-6, *E* and *Z*), 139.9 and 139.6 (s, ipso, *E* and *Z*), 129.1, 128.2, 127.6, 126.8, 126.0 (aroma), 51.7 and 50.9 (d, NC, *E* and *Z*), 43.9 (s, C-2, *E* and *Z*), 34.9 (t), 34.1 (t), 32.4 (t), 26.7 (q, C*Me*$_3$), 26.3 and 23.9 (q, CH*Me*$_2$, *Z* and *E*), 22.7 (t, C-5, *E*). Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.53; H, 9.69; N, 5.09.

***N*-(5-Butyl-2,2-dimethyl-3-oxo-6-heptylidene)isopropylamine (6df).** Obtained from **1d** and **5f** according to the general procedure by distillation: bp 80 °C/0.1 mmHg; IR (neat) 1700, 1660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.58 (septet, 1H, *J* = 6.35 Hz), 3.16 (dd, 1H, *J* = 17.82, 10.01 Hz), 2.69 (m, 1H), 2.36 (dd, 1H, *J* = 17.82, 4.15 Hz), 1.86 (s, 3H), 1.52–0.86 (m, 9H), 1.12 (s, 9H), 1.00 (d, 6H, *J* = 6.35 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 215.2, 168.2, 49.8, 44.3, 43.7, 39.8, 32.8, 29.4, 26.6, 23.4, 22.8, 17.6, 13.9; MS *m/z* 254 ($M^+ + 1$), 168 ($M^+ - t$-BuCO); HRMS calcd for $C_{16}H_{31}NO$ 253.2406, found *m/z* 253.2430 (M^+).

***N*-(2,2-Dimethyl-3-oxo-5-pentyl-6-hexylidene)isopropylamine (6dg).** Obtained from **1d** and **5g** according to the general procedure by distillation: bp 110 °C/0.1 mmHg; IR (neat) 1710, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.65 (d, 1H, *J* = 4.88 Hz), 3.24 (septet, 1H, *J* = 6.35 Hz), 2.88 (dd, 1H, *J* = 17.09, 7.82 Hz), 2.81–2.73 (m, 1H), 2.48 (dd, 1H, *J* = 17.09, 5.37 Hz), 1.5–0.78 (m, 11H), 1.14 (s, 9H), 1.10 (d, 6H, *J* = 6.35 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 214.6, 164.1, 61.1, 44.0, 39.2, 39.1, 32.3, 31.8, 26.7, 26.5, 24.0, 22.5, 13.9; MS *m/z* 253 (M^+), 196 ($M^+ - C_4H_9$); HRMS calcd for $C_{16}H_{31}NO$ 253.2406, found *m/z* 253.2434 (M^+).

General Procedure for Synthesis of Substituted Pyrroles (9). A mixture of a tin enolate (3.6 mmol) and an additive (5.4 mmol) in dry solvent (3 mL) was stirred for 10 min under nitrogen. To this solution was added an α-haloimine (3.0 mmol), and the mixture was stirred under the reaction conditions noted in Table 7. Volatiles were removed under reduced pressure, diethyl ether (100 mL) and aqueous NH_4F (15%; 40 mL) were added, and the resulting Bu_3SnF was filtered off. The filtrate was washed with water (50 mL × 2), dried ($MgSO_4$), and evaporated. Flash chromatography of the resultant residue on silica gel gave the substituted pyrrole **9**.

3-Butyl-1-isopropyl-2,5-dimethylpyrrole (9af). Obtained from **1a** and **5f** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 99:1): IR (neat) 2920, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 5.65 (s, 1H), 4.38 (septet, 1H, *J* = 7.32 Hz), 2.32 (t, 2H, *J* = 7.81 Hz), 2.26 (s, 3H), 2.18 (s, 3H), 1.53–1.15 (m, 4H), 1.45 (d, 6H, *J* = 7.32 Hz), 0.91 (t, 3H, *J* = 7.32 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 126.0, 123.0, 119.3, 106.8, 47.0, 33.7, 25.9, 22.8, 22.3, 14.04, 14.00, 11.1; MS *m/z* 193 (M^+), 150 ($M^+ - C_3H_7$); HRMS calcd for $C_{13}H_{23}N$ 193.1830, found *m/z* 193.1840 (M^+). Anal. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.24. Found: C, 80.61; H, 11.64; N, 6.93.

1-Isopropyl-5-methyl-3-pentylpyrrole (9ag). Obtained from **1a** and **5g** according to the general procedure by distillation: bp 75 °C/1 mmHg; IR (neat) 2900, 1660, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 6.43 (s, 1H), 5.71 (s, 1H), 4.18 (septet, 1H, *J* = 6.83 Hz), 2.40 (t, 2H, *J* = 7.81 Hz), 2.19 (s, 3H), 1.58–1.13 (m, 6H), 1.37 (d, 6H, *J* = 6.83 Hz), 0.89 (t, 3H, *J* = 7.32 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 127.2, 123.2, 111.9, 106.4, 46.6, 32.0, 31.0, 27.3, 23.6, 22.6, 14.1, 12.0; MS *m/z* 193 (M^+), 150 ($M^+ - C_3H_7$); HRMS calcd for $C_{13}H_{23}N$ 193.1830, found *m/z* 193.1840 (M^+).

1-Isopropyl-5-phenyl-3-pentylpyrrole (9bg). Obtained from **1b** and **5g** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 4:1): IR (neat) 2900, 1710, 770 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 7.4–7.1 (m, 5H), 6.63 (s, 1H), 5.98 (s, 1H), 4.43 (septet, 1H, *J* = 6.59 Hz), 2.49 (t, 2H, *J* = 7.36 Hz), 1.7–1.1 (m, 6H), 1.36 (d, 6H, *J* = 6.59 Hz), 0.91 (t, 1H, *J* = 5.94 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 134.2, 133.7, 129.0, 128.2, 126.5, 124.6, 114.4, 108.7, 47.0, 32.0, 30.8, 27.4, 24.0, 22.6, 14.1; MS *m/z* 255 (M^+), 212 ($M^+ - 43$); HRMS calcd for $C_{18}H_{25}N$ 255.1987, found *m/z* 255.1974 (M^+). Anal. Calcd for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.88; H, 10.11; N, 5.55.

1-Isopropyl-3-pentyltetrahydrobenzopyrrole (9cg). Obtained from **1c** and **5g** according to the general procedure by flash chromatography (eluted by hexane): IR (neat) 2900, 1700, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 6.39 (s, 1H), 4.14 (septet, 1H, *J* = 6.84 Hz), 2.52 (t, 2H, *J* = 6.11 Hz), 2.43 (t, 2H, *J* = 6.11 Hz), 2.35 (t, 2H, 7.81 Hz), 1.84–1.70 (m, 4H), 1.58–1.51 (m, 2H), 1.49–1.39 (m, 4H), 1.36 (d, 6H, *J* = 6.84 Hz), 0.90 (t, 3H, *J* = 6.83 Hz); ^{13}C NMR (22.6 MHz, $CDCl_3$) 126.7, 121.2, 115.7, 111.0, 46.3, 32.1, 30.2, 25.7, 23.7, 23.6, 23.5, 22.6, 22.1, 21.7, 14.1; MS *m/z* 233 (M^+), 190 ($M^+ - C_3H_7$); HRMS calcd for $C_{16}H_{27}N$ 233.2143, found *m/z* 233.2129 (M^+). Anal. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00. Found: C, 82.53; H, 11.80; N, 5.79.

1-Isopropyl-2-*tert*-butyltetrahydrobenzopyrrole (9ca). Obtained from **1c** and **5a** according to the general procedure by flash chromatography (eluted by hexane-diethyl ether, 1:1): IR (neat) 2930, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 5.65 (s, 1H), 4.76 (septet, 1H, *J* = 6.84 Hz), 2.73 (t, 2H, *J* = 6.11 Hz), 2.50 (t, 2H, *J* = 6.34 Hz), 1.83–1.67 (m, 4H), 1.46 (d, 6H, *J* = 6.84 Hz), 1.36 (s, 9H); ^{13}C NMR (22.6 MHz, $CDCl_3$) 139.6, 127.4, 116.4, 102.8, 47.4, 32.0, 31.3, 25.4, 24.2, 23.5, 23.3, 22.1; MS *m/z* 219 (M^+), 162 ($M^+ - C_4H_9$); HRMS calcd for $C_{15}H_{25}N$ 219.1987, found *m/z* 219.1971 (M^+).

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Supplementary Material Available: Characterization data for **3ca, 10, 3ba–1, 5b, 5c, 5f, 5g, 6aa, 6ba, 6ca, 6da, 6ab, 6ac, 6dc, 6be, 6de, 6df, 6dg, 9af, 9ag, 9bg, 9cg**, and **9ca** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.