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Kinetics of Intramolecular Additions of the Aminyl Radicals to Carbonyl Groups and Subsequent Ring Openings

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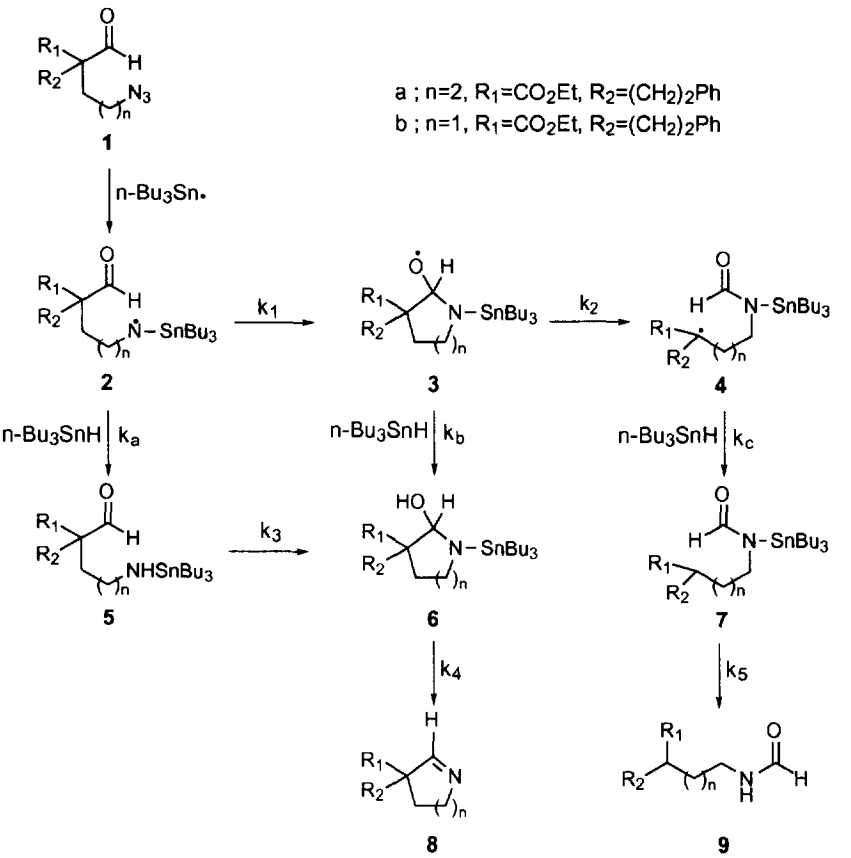
Abstract : The rates of cyclizations of the aminyl radicals were measured (**2a** : $k_1 = 5.1 \times 10^5\ s^{-1}$, **2b** : $k_1 = 3.1 \times 10^4\ s^{-1}$). The angle strains slow down the ring closures. The cyclized oxy radicals **3a** and **3b** then undergo β-scission to give **4a** and **4b** with the rates (**3a** : $k_2 = 6.5 \times 10^8\ s^{-1}$, **3b** : $k_2 = 1.0 \times 10^7\ s^{-1}$).

Recently Kim et al[1] have reported that additions of n-Bu_3Sn· to the aldehydoazides **1**, generate the aminyl radials, **2**, which then add onto the carbonyl group to give the oxy radicals **3**. **3** could fragment to **4**. The intermediates **3** and **4** may also react with n-Bu_3SnH to produce **8** and **9** via **6** and **7**, respectively. (refer to Scheme 1) At elevated temperatures, i.e. 80℃, **1** was reduced to the corresponding amine by n-Bu_3SnH, which can be condensed to afford **8**. The formation of **8** via the condensation was however practically nil at 25°C. The aminyl radicals[2] add reversively[3] to simple C=C bonds in spite of favorable enthalpic term, i.e. ΔH= - 17 kcal/mol for CH_2=CH_2 + NH_2· $\rightleftharpoons$ ·$CH_2CH_2NH_2$. The cyclizations[4-6] of the aminyl radicals still seem to be reversible although the intramolecular additions gain entropic advantage[7] relative to their intermolecular counterparts. The aminyl radicals however undergo facile cyclizations with suitably activated alkenes[8, 9] and exhibit nucleophilic character. The nucleophilicity[10] of the aminyl radicals **2**, could be thereby augmented with the highly polarized carbonyl group for the formations of **3**. **3** can be then readily scavenged via either the hydrogen transfer ($k_b = 2 \times 10^8 M^{-1}s^{-1}$ at 22 ℃)[11] or the ring openings ($k_2 \simeq 10^7$-$10^8\ s^{-1}$ at 25 ℃ : Table 2). The decomposition of **3** back to **2** can be therefore efficiently minimized to pronounce the additions (k_1) as irreversible process.[12] We now wish to report and discuss the kinetic data regarding the cyclizations of the aminyl radicals, followed by the ring openings.

Scheme 1



Product Formations Derived from the Photolysis.

The ampoules containing the aldehydoazides **1** (0.01-0.05M) and n-Bu_3SnH (0.07-0.9M) dissolved in benzene, were prepared by freeze-pump-thaw method. Seven to eighteen-fold excess of n-Bu_3SnH was used relative to quantities of **1** to guarantee the pseudo-first order kinetics. The ampoules were then photolysed with the Hanovia lamp (for 350 nm) at 25 °C to obtain **8** and **9** as the final products. Previously[1], n-Bu_3SnH was added very slowly to **1** to maintain high dilution conditions, which could efficiently minimize the formation of **8**. Present reactions employ relatively large concentrations of n-Bu_3SnH, thereby producing comparable amounts of **8** and **9**. **8** has been formed via two pathways involving **3** and **5**. **3** may also fragment to **4** leading to formation of **9** via **7**. The products (**8** and **9**) were measured by NMR method to account for ca. 95% of the starting azides (refer to Table 1).

Table 1. Distributions and Ratios of the Products from the Reactions of **1** with n-Bu_3SnH at 25°C in Benzene

$[\mathbf{1a}]_0$[a]	$[Bu_3SnH]_0$[a]	[**8a**][b]	[**9a**][b]	[**8a**]/[**9a**]	$[\mathbf{1b}]_0$[a]	$[Bu_3SnH]_0$[a]	[**8b**][b]	[**9b**][b]	[**8b**]/[**9b**]
0.05	0.90	0.010	0.035	0.286	0.03	0.30	0.024	0.0025	9.6000
0.05	0.70	0.0097	0.036	0.269	0.03	0.21	0.023	0.0036	6.3889
0.05	0.50	0.0065	0.040	0.163	0.01	0.14	0.0076	0.0019	4.0000
0.05	0.35	0.0048	0.042	0.114	0.01	0.10	0.0070	0.0028	2.5000
					0.01	0.07	0.0059	0.0037	1.5946

a. Initial reactant concentrations in mol/L. b. All the products were identified and quantified by comparison with authentic samples, and concentrations in mol/L.

Measurements of the Rate Constants.

The compounds **5**, **6**, and **7** were never isolated and considered to be very unstable for isolation. Applying steady-state approximations to concentrations of the intermediates (**3**, **4**, **5**, **6**, and **7**) and the aforementioned pseudo-first-order kinetics, the product ratios, [**8**]/[**9**] were related with initial concentrations of n-Bu_3SnH as with eq 1.[13]

$$\frac{[\mathbf{8}]}{[\mathbf{9}]}\frac{1}{[\text{n-Bu}_3\text{SnH}]_0^2} = \frac{k_a k_b}{k_1 k_2} + \frac{k_a k_2 + k_b k_1}{k_1 k_2}\frac{1}{[\text{n-Bu}_3\text{SnH}]_0} \qquad (1)$$

Table 1 shows various product ratios, [**8**]/[**9**] with different initial concentrations of n-Bu_3SnH. Since $[\text{n-Bu}_3\text{SnH}]_o$ stays almost constant throughout the reactions, plots of $[\mathbf{8}]/[\mathbf{9}][\text{n-Bu}_3\text{SnH}]_o^2$ against $1/[\text{n-Bu}_3\text{SnH}]_o$ must yield straight lines where the intercepts correspond to k_ak_b/k_1k_2 and the slopes, $(k_ak_2+k_bk_1)/k_1k_2$. The data of Table 1 were fitted into eq. 1 to produce Figures 1 and 2.

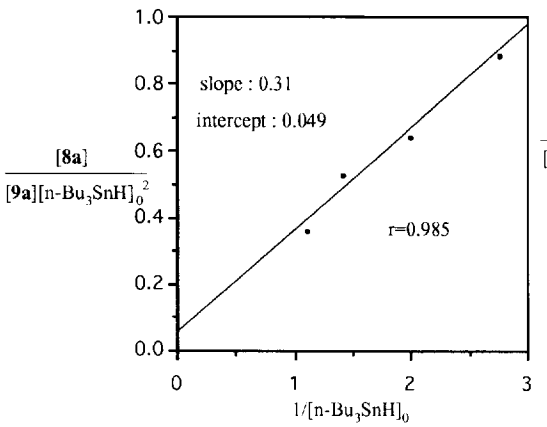


Figure 1

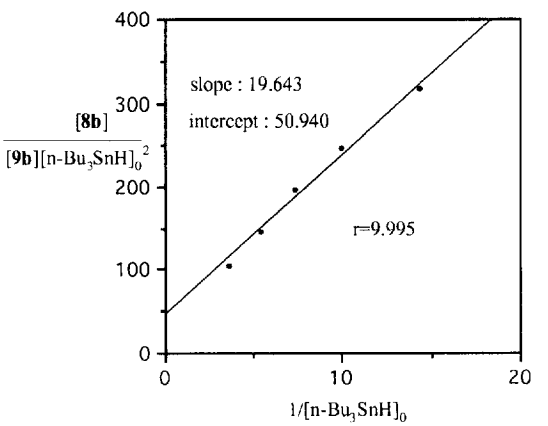


Figure 2

Taking $k_a/k_1=x$, $k_b/k_2=y$, $[\mathbf{8}]/[\mathbf{9}][n\text{-}Bu_3SnH]_o^2=A$, and $1/[n\text{-}Bu_3SnH]_o=B$, eq 1 can be written down as

$$A = xy + (x + y)\,B \qquad (2)$$

A and B were experimentally determined from Table 1. xy and x + y correspond to the intercept and slope, respectively in Figures 1 and 2. The values of $x = k_a/k_1$ and $y = k_b/k_2$ have been thereby computed. Although Figure 1 indicates intercept (xy) = 0.049 and slope (x + y) = 0.310, x and y cannot be solved to give real numbers. Figure 2 shows intercept (xy) = 50.940 and slope (x + y) = 19.643, which were solved to yield x = 3.075 and y = 16.568. $k_1 = 2.6 \times 10^4\ s^{-1}$ for **2b** and $k_2 = 1.2 \times 10^7\ s^{-1}$ for **3b** were thereby determined from the known values of k_a[14] $= 8 \times 10^4\ M^{-1}s^{-1}$ at 50 °C and k_b[11] $= 2.0 \times 10^8\ M^{-1}s^{-1}$ at 22 °C (refer to Table 2).

Table 2. Rate Constants for Cyclizations of **2** and Ring Openings of **3** at 25 °C in Benzene.

Substrates	k_1[a] (s^{-1})	$k_2\ (s^{-1})$
1a	[b] $(5.1 \pm 1.7) \times 10^5$	[b] $(6.5 \pm 0.1) \times 10^8$
1b	[b] $(3.1 \pm 0.3) \times 10^4$	[b] $(1.0 \pm 0.1) \times 10^7$
	[c] $(2.6 \pm 0.2) \times 10^4$	[c] $(1.2 \pm 0.1) \times 10^7$

a. The values could be somewhat crude because the k_a of k_a/k_1 is not available for Scheme 1. k_a was therefore borrowed from another reaction.[14] b. Calculated using eq 3 c. Calculated using eq 1

Assuming $k_ak_2 \ll k_bk_1$, eq 1 could be approximated to eq 3.

$$\frac{[\mathbf{8}]}{[\mathbf{9}]}\,\frac{1}{[n\text{-}Bu_3SnH]_o^2} = \frac{k_ak_b}{k_1k_2} + \frac{k_b}{k_2}\,\frac{1}{[n\text{-}Bu_3SnH]_o} \qquad (3)$$

The data of Table 1 then could similarly give rise to straight lines with eq 3. The intercept ($k_ak_b/k_1k_2 = 4.9 \times 10^{-2}\ M^{-2}$) and slope ($k_b/k_2 = 3.1 \times 10^{-1}\ M^{-1}$) have been determined for the reactions of **1a** to give $k_1 = 5.1 \times 10^5\ s^{-1}$ for **2a** and $k_2 = 6.5 \times 10^8\ s^{-1}$ for **3a**. The magnitude of $k_2 = 6.5 \times 10^8\ s^{-1}$ appears reasonable because $[\mathbf{8a}]/[\mathbf{9a}] < 1$ in Table 1 demands that fragmentation of **3a** should take place faster than the hydrogen abstractions by **3a** that is $k_2 > k_b[n\text{-}Bu_3SnH]_0$. However, the combination of $k_1 = 5.1 \times 10^5\ s^{-1}$ and $k_2 = 6.5 \times 10^8 s^{-1}$ barely satisfies the assumption ($k_ak_2 \ll k_bk_1$). This suggests that $k_1 = 5.1 \times 10^5\ s^{-1}$ may represent the lower limit for the effective k_1 value. $k_1 = 3.1 \times 10^4\ s^{-1}$ for **2b** and $k_2 = 1.0 \times 10^7\ s^{-1}$ for **3b** were also similarly computed from $k_ak_b/k_1k_2 = 5.09 \times 10\ M^{-2}$ and $k_b/k_2 = 1.96 \times 10\ M^{-1}$, which were derived from a straight line. The value of $k_2 = 1.0 \times 10^7\ s^{-1}$ also satisfies $k_2 < k_b[n\text{-}Bu_3SnH]_o$, which could account for the ratio, $[\mathbf{8b}]/[\mathbf{9b}] > 1$. The rate constants ($k_1$ and k_2) calculated with the eq 3 are thus included in Table 2. The rate constants for the reactions of **1b** maintain very comparable magnitude whether obtained from either eq 1 or eq 3. This may strongly justify the foregoing assumption ($k_ak_2 \ll k_bk_1$) and validate eq 3.

Enthalpic vs. Entropic Contributions to the Rates of the Ring Closures and Openings.

The rates of radical additions[15] result from the complex interplay of polar, steric, and bond-strength

terms. The intramolecular additions that is cyclizations' could be further influenced by the angle strains and stereoelectronic effects. The various enthalpic elements could be incorporated with different weights into an enthalpy of activation ($\Delta H^{\ddagger}$) , which is to be combined with an entropic term ($\Delta S^{\ddagger}$) to produce a rate. The cyclizations of ω-alkenyl radicals[16] preferentially take anti-Markovnikov mode to give thermodynamically less stable products. The rate of the exo ring closure ($k = 2 \times 10^5 s^{-1}$ at 25 °C) is therefore much faster than that of endo counterpart ($k = 4 \times 10^3 s^{-1}$ at 25 °C) for 5-hexenyl radical. When the cyclization takes place via the "early"[17]transition state (TS), the heat of reaction and angle strains could not seriously influence the rates. Stereoelectronic effect [16]is an enthalpic term and has been nominated to be the prime candidate favoring the exo cyclization of 5-hexenyl radical. Pentenoxy radical[18] cyclizes to yield a five-membered ring rather than a six-membered one due to the favorable entropic effects. The similar entropic effects may additionally contribute to boost the rate of the exo cyclization.

The ring closures of ω-formylalkyl radicals[19] display two distinct features not observed with the reactions of ω-alkenyl radicals.[16] The cyclizations could occur via the exo mode only. The stereoelectronic effects[16] and entropic contributions[18] therefore could be no more the rate-differentiating elements. The C=O bond of ω-formylalkyl radicals also maintains much stronger polarity than C=C bond of ω-alkenyl radicals. Since ω-formylalkyl radicals may assume nucleophilic character, the TS leading to the cyclization of ω-formylalkyl radicals could be accordingly classified as "late"[17] one which resembles the cyclized ring skeleton to experience the substantial angle strains. The angle strains thereby eminently explain why the rate of the ring closure of 5-formylpentyl ($k = 2.5 \times 10^5 s^{-1}$ at 25 °C) is slightly faster than that of 4-formylbutyl ($k = 1.5 \times 10^5 s^{-1}$ at 25 °C) radicals. The same angle strains however accelerate the ring openings also so that cyclo-pentyloxy radical ($k = 9.1 \times 10^7 s^{-1}$ at 25 °C) undergoes the fragmentation faster than cyclo-hexyloxy radical ($k = 2.1 \times 10^6 s^{-1}$ at 25 °C).

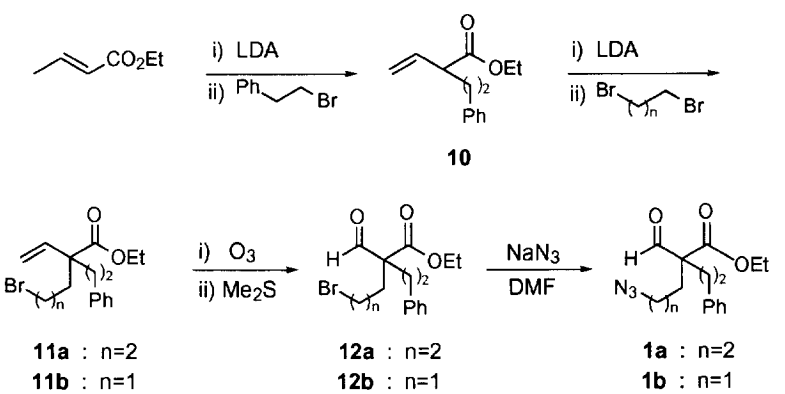
The rates of the 6-exo ring closure of **2a** ($k_1 = 5.1 \times 10^5 s^{-1}$) and the 5-exo ring closure of **2b** ($k_1 = 3.1 \times 10^4 s^{-1}$) also obey the angle strains. The angle strains however can hardly explain the rates of the subsequent ring openings. Six-membered ring (**3a** : $k_2 = 6.5 \times 10^8 s^{-1}$) fragments faster than five-membered one (**3b** : $k_2 = 1.0 \times 10^7 s^{-1}$). The cyclizations of ω-formylalkyl radicals[19] involve "late" TS to yield the cycloalkyloxy radicals. The reverse reaction that is the ring openings accordingly take "early" TS and produce primary alkyl radicals. However, the ring openings of **3a** and **3b** give rise to however the formation of tertiary alkyl radicals which are relatively stable than the primary structures. The TS for the fragmentations of **3a** and **3b** may therefore involve significant bond breakings to yield the "late" TS whose structure approaches to that of the products **4a** and **4b**. The reaction parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) may seriously influence the corresponding activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) when the TS resembles the product structure (an extension of the Hammond Postulate)[17]. **4a** contains one more carbon atom than **4b** whereby the former could undergo more internal motions such as the rotations and vibrations. According to the " Additivity Rules for Molecular Properties",[20] the entropy of reaction during the fragmemtation of **3a** to **4a** should be larger than in case of **3b** and **4b.** The former reaction enjoys accordingly the larger entropy of activation than the latter. The two ring openings may however involve comparatively similar heat of reactions. The statements concerning the entropies therefore rationalize that **3a** ($k_2 = 6.5 \times 10^8 s^{-1}$) should fragment faster than **3b** ($k_2 = 1.0 \times 10^7 s^{-1}$).

Conclusions

The cyclization of ω-alkenyl radicals involves "early" TS. The stereoelectronic effects thereby seriously outweigh the angle strians to explain the much faster rates of the exo cyclizations than those of the endo modes. The ring closures of ω-formylalkyl radicals and **2** could traverse "late" TS whereby the rates are controlled albeit to a lesser extent by the angle strains. Depending upon the stabilities of the products that is the open alkyl radicals, the cycloalkyloxy radical may undergo ring openings via either "early" or "late" TS. The "early" TS may experience the angle strains which differentiate the rates of the openings. The "late" TS could be immune from the angle strains and the rates of the β-scissions are controlled by the entropies derived from the internal motions. Since the cyclizations are the reverse processes of the openings, the cyclizations may lose such internal degrees of freedom, which appear to be the reason for the tardy rates of the cyclizations forming larger than six-membered rings.

Experimental

General Scheme for Preparations of the Azido Aldehydes (1a, 1b)



Ethyl 2-(2-phenylethyl) crotonate (10). A mixture of diisopropylamine (1.01 g, 10 mmol) and n-BuLi (1.4 M solution in hexane, 7.1 ml, 10 mmol) in THF (10 ml) was stirred for 1h at -78 ℃. Then, HMPA (1.79g, 10 mmol) was added to the solution of LDA, and the reaction mixture was stirred for 30 min at -78 ℃. To the reaction mixture was added a solution of ethyl crotonate (1.37 g, 11 mmol) in THF (3 ml) at -78 ℃. After 1h at that temperature, a solution of 2-bromoethylbenzene (1.85 g, 10 mmol) in THF (3 ml) was added dropwise to the reaction mixture. After addtional stirring for 5h at -78°C, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. After distillation using Kugelrohr (100-105 °C/1 mmHg) and silica gel column chromatography, **10** (1.04g, 48%) was obtained as a colorless oil : **^{1}H NMR** (200MHz, $CDCl_3$) δ 7.1-7.3 (m,

5H), 5.8-6.0 (m, 1H), 5.1-5.2 (m, 2H), 4.17 (q, 2H), 3.05 (q, 1H), 2.5-2.7 (m, 2H), 2.0-2.2 (m, 1H), 1.8-2.0 (m, 1H), 1.26 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 173.7, 141.4, 135.9, 128.4, 128.3, 125.9, 117.4, 60.5, 49.7, 33.6, 33.2, 14.2 ppm. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{14}H_{19}O_2$: 219.1385. Found: 219.1378.

Ethyl 2-(2-phenylethyl)-5-bromo-2-vinyl-pentanoate (11a). The similar procedure afforded **11a** (824 mg, 78%) using crotonate **10** (694 mg, 3.18 mmol) and dibromopropane (834 mg, 4.13 mmol) : **^{1}H NMR** (200MHz, $CDCl_3$) δ 7.1-7.3 (m, 5H), 6.03 (dd, 1H), 5.23 (dd, 2H), 4.15 (q, 2H), 3.38 (t, 2H), 2.5-2.7 (m, 2H), 1.8-2.0 (m, 6H), 1.27 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 174.7, 142.0, 139.3, 128.4, 128.3, 125.9, 115.2, 60.8, 51.8, 38.4, 34.7, 33.9, 30.8, 27.8, 14.3 ppm. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{17}H_{24}BrO_2$: 339.0960. Found: 339.0950.

Ethyl 2-(2-phenylethyl)-4-bromo-2-vinyl-butyrate (11b). The similar procedure afforded **11b** (1.28 g, 80%) using crotonate **10** (1.05 g, 4.90mmol) and dibromoethane (549 mg, 6.37 mmol) : **^{1}H NMR** (200MHz, $CDCl_3$) δ 7.1-7.3 (m, 5H), 6.05 (dd, 1H), 5.24 (dd, 2H), 4.17 (q, 2H), 3.34 (t, 2H), 2.3-2.6 (m, 4H), 2.01 (t,2H), 1.28 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 173.8, 141.6, 138.3, 128.5, 128.3, 126.0, 115.7, 61.1, 52.8, 39.6, 38.9, 30.7, 27.8, 14.2 ppm. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{16}H_{22}BrO_2$: 325.0803. Found: 325.0798.

Ethyl 2-(2-phenylethyl)-5-bromo-2-formyl-pentanoate (12a). A solution of **11a** (600 mg, 1.77 mmol) in CH_2Cl_2 (10 ml) was cooled to -78℃. Ozone was bubbled through the solution until a bule color developed. After 5min, dimethyl sulfide (1 ml) was added. The reaction mixture was gradually warmed to room temperature. After being stirred for 24 h, the solvent was evaporated. After purification by silica gel column chromatography, **12a** (508 mg, 84%) was obtained : **^{1}H NMR** (200MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.1-7.3 (m, 5H), 4.26 (q, 2H), 3.36 (t, 2H), 2.2-2.6 (m, 2H), 1.7-2.2 (m, 6H), 1.31 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 199.9, 171.5, 140.9, 128.5, 128.3, 126.3, 61.6, 60.4, 34.8, 33.1, 31.0, 30.6, 27.5, 14.2 ppm. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{16}H_{21}BrO_3$: 341.0752. Found: 341.0746.

Ethyl 2-(2-phenylethyl)-4-bromo-2-formyl-butyrate (12b). The similar procedure as described for the preparation of **12a** afforded **12b** (864mg, 87%) using crotonate **11b** (990mg, 3.04mmol) : **^{1}H NMR** (200MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.1-7.3 (m, 5.H), 4.28 (q. 2H), 3.2-3.4 (m, 2H), 2.4-2.6 (m, 4H), 2.1-2.3 (m, 2H), 1.31 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 199.0, 170.8, 140.4, 128.6, 128.2, 126.4, 61.9, 61.1, 35.7, 35.3, 30.5, 26.7, 14.2 ppm. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{15}H_{19}BrO_3$: 327.0596. Found: 327.0583.

Ethyl 2-(2-phenylethyl)-5-azido-2-formyl-pentanoate (1a). To a DMF (3ml) solution of **12a** (500mg,1.47 mmol) was added NaN_3 (287 mg, 4.41mmol) and stirred for 10 h at room temperature. After addtion of brine (5ml), the aqueous layer was extracted with diethyl ether (20 ml × 4) and the combined organic layer was washed with water (10 ml × 2). The resultant organic layer was dried, filtered, and evaporated. After purification by silica gel column chromatography, **1a** (308 mg, 69%) was obtained : **^{1}H NMR** (200MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.1-7.3 (m, 5H), 4.26 (q, 2H), 3.27 (t, 2H), 2.4-2.6 (m, 2H), 2.0-2.2 (m,2H), 1.8-2.0 (m, 2H), 1.4-1.6 (m, 2H), 1.31 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 200.0, 171.6, 140.9, 128.5, 128.3, 126.3, 61.6, 60.5, 51.3, 35.0, 30.6, 29.6, 23.9, 14.2 ppm ; **IR** (NaCl) 2098, 1721 cm^{-1}. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{16}H_{22}N_3O_3$: 304.1661. Found: 304.1695.

Ethyl 2-(2-phenylethyl)-4-azido-2-formyl-butyrate (1b). To a DMF (5ml) solution of **12b** (850 mg, 2.60 mmol) was added NaN_3 (507 mg, 7.80 mmol) and stirred for 12 h at room temperature. Workup as described for the preparation of **1a** gave the azido aldehyde **1b** (489 mg, 65%) as a colorless oil : **^{1}H NMR** (200MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.1-7.3 (m, 5H), 4.32 (q.2H), 3.2-3.4 (m, 2H), 24-2.6 (m, 2H), 2.1-2.3 (m, 4H), 1.36 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 199.5, 171.2, 140.6, 128.6, 128.3, 126.4, 61.8, 53.9, 47.3, 35.7, 32.0,

30.6, 14.2 ppm ; **IR** (NaCl) 2100, 1720 cm^{-1}. **HRMS(CI)** m/z $(M+1)^+$; calcd for $C_{15}H_{20}N_3O_3$: 290.1505. Found: 290.1512.

Photolytic Reactions of Aldehydoazides (1a and 1b) with n-Bu$_3$SnH.

The azides (**1a** and **1b**) showed no reactions with n-Bu_3SnH at room temperature for 4 h although they were reduced to amines in refluxing benzene. The two reagents were combined and the photolysis were carried out in sealed and degasses Pyrex tubes. The initial concentrations of the azides and n-Bu_3SnH were 0.01-0.05 M and 0.07-0.90 M, respectively. For a typical experiment, an azid was weighed into a 5-ml volumetric flask. The flask was charged with benzene (4 ml) and the appropriate amount of n-Bu_3SnH (7, 10, 14 , and 18 equivalents of **1a** ; 7, 10, and 14 equivalents of **1b**). Finally, benzene was added to the mark. The solution was then transferred to several septum-sealed Pyrex tubes which were degassed and sealed by the freeze-pump-thaw method. The samples were then placed in a constant temperature water bath (± 1 °C) at 25 °C. After a 5-min equilibration, the reaction vessels were irradiated with a 450W high pressure mercury lamp from a distance of 10cm for 2 h. After evaporation of solvent, the products were analyzed by ^1H NMR (Bruker Fourier Transform AM300) spectrometer.

3-Phenethyl-4,5-dihydro-3H-pyrrole-3-carboxylic acid ethyl ester (8a) : ^1H NMR (200MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.1-7.3 (m, 5H), 4.18 (q, 2H), 3.4-3.8 (m, 2H), 2.5-2.6 (m, 2H), 2.2-2.4 (m, 1H), 2.0-2.2 (m, 1H), 1.8-2.0 (m, 1H), 1.5-1.8 (m, 3H), 1.27 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 172.7, 162.4, 141.1, 128.5, 128.2, 126.1, 61.2, 49.4, 48.6, 39.4, 30.5, 27.0, 19.7, 14.2ppm ; **IR** (NaCl) 1727, 1649 cm^{-1}. **HRMS(EI)** m/z (M^+); calcd for $C_{16}H_{21}NO_2$: 259.1572. Found: 259.1575.

3-Phenethyl-3,4,5,6-tetrahydro-pyridine-3-carboxylic acid ethyl ester (8b) : ^1H NMR (200MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.1-7.3 (m, 5H), 4.17 (q, 2H), 3.96 (t, 2H), 2.56 (t, 2H), 2.4-2.5 (m, 1H), 2.2-2.3 (m, 1H), 1.8-2.0 (m, 2H), 1.27 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 172.5, 166.6, 140.9, 128.4, 128.2, 126.1, 64.5, 61.3, 61.0, 37.5, 31.5, 31.1, 14.2 ppm ; **IR** (NaCl) 1728, 1624 cm^{-1}. **HRMS(EI)** m/z (M^+); calcd for $C_{15}H_{19}NO_2$: 245.1416. Found: 245.1414.

4-Formylamino-2-phenethyl-butylic acid ethyl ester (9a) : ^1H NMR (200MHz, $CDCl_3$) δ 8.11 (transe = s, cis = d, 1H), 7.1-7.3 (m, 5H), 5.74 (br s, 1H), 4.11 (q, 2H), 3.27 (q, 2H), 2.5-2.7 (m, 2H), 2.3-2.5 (m, 1H), 1.8-2.0 (m, 1H), 1.6-1.8 (m, 2H), 1.4-1.6 (m, 3H), 1.26 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 175.8, 161.2, 141.4, 128.4, 128.3, 126.0, 60.4, 44.7, 37.8, 34.1, 33.5, 29.4, 27.2, 14.3 ppm ; **IR** (NaCl) 3312, 1727, 1670 cm^{-1}. **HRMS(EI)** m/z (M^+); calcd for $C_{16}H_{23}NO_3$: 277.1678. Found: 277.1655.

5-formylamino-2-phenethyl-pentanoic acid ethyl ester (9b) : ^1H NMR (200MHz, $CDCl_3$) δ 8.10 (transe = s, cis = d, 1H), 7.1-7.3 (m, 5H), 5.73 (br s, 1H), 4.17 (q, 2H), 3.2-3.5 (m, 2H), 2.5-2.7 (m, 2H), 2.4-2.5 (m, 1H), 1.7-2.0 (m, 4H), 1.26 (t, 3H) ; **^{13}C NMR** ($CDCl_3$) 175.6, 161.1, 141.2, 128.4, 128.3, 126.0, 60.6, 42.7, 36.2, 33.9, 33.4, 31.6, 14.3 ppm ; **IR** (NaCl) 3310, 1725, 1670 cm^{-1}. **HRMS(EI)** m/z (M^+); $C_{15}H_{21}NO_3$: 263.1533. Found: 263.1512.

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13. The rates of formation of **8** and **9** can be expressed as follows

$$d[8] / dt = k_4[6] \quad ; \quad d[9] / dt = k_5 [7]$$

The application of steady-state approximations to [6] and [7] gives rise to

$$d[8] / dt = k_3[5] + k_b[3] [n\text{-}Bu_3\ SnH]_0$$

$$d[9] / dt = k_c[4] [n\text{-}Bu_3SnH]_0$$

When [5] follows steady-state approximations,

$$d[8] / dt = k_a[2] [n\text{-}Bu_3SnH]_0 + k_3[3] [n\text{-}Bu_3SnH]_0$$

When d[8] / dt is divided by d[9] / dt,

$$\frac{d[8]}{d[9]} = \frac{k_a[2] + k_b[3]}{k_c[4]}$$

The steady-state approximations for [3] and [4] yield

$$\frac{d[8]}{d[9]} = \frac{k_a (k_2 + k_b[n\text{-}Bu_3SnH]_0) / k_1 + k_b}{k_2 / [n\text{-}Bu_3SnH]_0}$$

The integrations may finally bring about eq 1 as follows

$$\frac{[8]}{[9]}\frac{1}{[\text{n-Bu}_3\text{SnH}]_0^2} = \frac{k_a k_b}{k_1 k_2} + \frac{k_a k_2 + k_b k_1}{k_1 k_2}\frac{1}{[\text{n-Bu}_3\text{SnH}]_0}$$

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