Notes

Allylic Amination by the Lewis-Acid-Mediated Ene Reaction of Diethyl Azodicarboxylate with Alkenes

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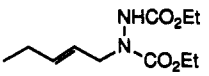
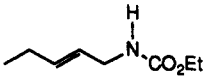
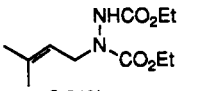
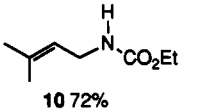
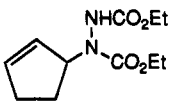
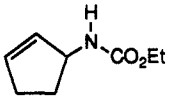
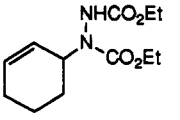
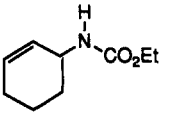
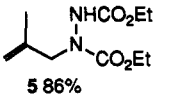
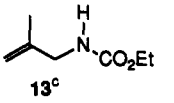
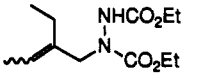
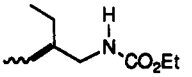
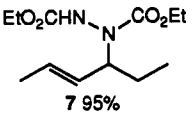
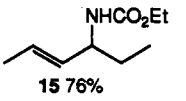
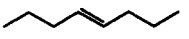
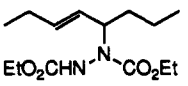
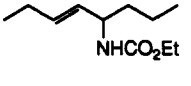
The ene reaction[2] plays an important role in organic synthesis as a method for carbon–carbon bond formation. Because there are a variety of enophiles available, the ene reaction converts readily accessible alkenes into more functionalized compounds in which the double bond undergoes allylic transposition. For example, the use of an aldehyde as enophile, the so called "carbonyl–ene" reaction now constitutes a useful method for construction of carbon skeletons. This is particularly so due to the recent development of chiral Lewis acid catalysts which have extended this reaction in an asymmetric sense.[3]

Use of azo compounds such as diethyl azodicarboxylate (DEAD) as enophiles provides a useful method for allylic amination of alkenes. Until recently, the preparation of allylic amines was limited to the use of sulfur or selenium diimido compounds,[4] *N*-sulfinylbenzenesulfonamide,[5] N-phenyl-1,2,4-triazoline,[6] or acylnitroso compounds.[7] Although the thermal ene reaction of DEAD with various alkenes has been reported,[8] the reactions generally require elevated temperature and are plagued by the formation of diadducts. Leblanc *et al.*[9] improved this thermal azo–ene reaction by using the more reactive enophile bis(2,2,2-trichloroethyl) azodicarboxylate furnishing the free allylic amines upon reduction of the ene adducts using zinc in acetic acid.

Despite the widespread use of Lewis acid to catalyze the "carbonyl–ene" and "imine–ene" reactions,[3,10] Lewis acid catalysis of the analogous "azo–ene" reaction has received little attention. We therefore wish to report our studies on the Lewis-acid catalyzed reaction of diethyl azodicarboxylate with various substituted alkenes.

Table I

alkene	ene adduct[a]	carbamate[b]
	 **1** 87% (*E*:*Z*, 11:1)	 **9** 86% (*E*:*Z*, 11:1)
	 **2** 91%	 **10** 72%
	 **3** 85%	 **11** 74%
	 **4** 77%	 **12** 72%
	 **5** 86%	 **13**[c]
	 **6** 84% (*E*:*Z*, 2:1)	 **14** 67% (*E*:*Z*, 2:1)
	 **7** 95%	 **15** 76%
	 **8** 80%	 **16** 71%

[a] $EtO_2CN{=}NCO_2Et$ (1.0 equiv), alkene (2.0 equiv), $SnCl_4$ (1.0 equiv), –60 °C, 5 min, CH_2Cl_2. [b] Li (5.0 equiv), liquid NH_3, –33 °C, 1 h, then NH_4Cl (10 equiv). [c] This compound was not isolated because of its volatility.

Initial attempts to catalyze the ene reaction of 1-pentene with DEAD using Et_2AlCl or Me_2AlCl in toluene at –78 °C resulted in transfer of the alkyl group on the Lewis acid to the azo compound. Use of $BF_3{\cdot}Et_2O$, Et_2BBr, and $ZnBr_2$ effected no reaction at room temperature while $Ti(O^iPr)_4$ resulted in reduction of the azo compound to the hydrazine. Success, however, was finally realized in the reaction of various alkenes (Table I) with DEAD using $SnCl_4$ (1.0 equiv) in dichloromethane. In this case, the reactions were complete in several minutes at –60 °C, affording the ene adducts in 77–95% yield after purification by flash chromatography. Two equivalents of

(1) Current address: Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand.

(2) For reviews on the ene reaction, see: (a) Hoffmann, H. M. R. *Angew Chem. Int. Ed. Engl.* **1969**, *8*, 556. (b) Oppolzer, W.; Snieckus, V. *Angew Chem. Int. Ed. Engl.* **1978**, *17*, 476.

(3) For a review of asymmetric ene reactions, see: Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021.

(4) (a) Kresze, G.; Munsterer, H. *J. Org. Chem.* **1983**, *48*, 3561. (b) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. L. *J. Am. Chem. Soc.* **1976**, *98*, 269. (c) Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1448.

(5) Deleris, G.; Dunogues, J.; Gadras, A. *Tetrahedron* **1988**, *44*, 4243.

(6) Hoye, T. R.; Bottoroff, K. J.; Caruso, A. J.; Dellaria, J. F. *J. Org. Chem.* **1980**, *45*, 4287.

(7) Keck, G. E.; Webb, R. R.; Yates, J. B. *Tetrahedron* **1981**, *37*, 4007.

(8) (a) Huisgen, R.; Pohl, H. *Chem. Ber.* **1960**, *93*, 527. (b) Thaler, W. A.; Franzus, B. *J. Org. Chem.* **1964**, *29*, 2226. In addition, certain simple alkenes, such as enol ethers, undergo [4 + 2] cycloaddition reactions with DEAD. For a leading reference, see: (c) Fitzsimmons, B. J.; Leblanc, Y.; Rokach, J. *J. Am. Chem. Soc.* **1987**, *109*, 285.

(9) Leblanc, Y.; Zamboni, R.; Bernstein, M. A. *J. Org. Chem.* **1991**, *56*, 1971.

(10) (a) Achmatowicz, O.; Pietraszkiewicz, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2680. (b) Tschaen, D. M.; Weinreb, S. M. *Tetrahedron Lett.* **1982**, *23*, 3015. (c) Tschaen, D. M.; Turos, E.; Weinreb, S. M. *J. Org. Chem.* **1984**, *49*, 5058. (d) Braxmeier, H.; Kresze, G. *Synthesis* **1985**, 683.

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alkene were used in order to minimize the formation of diadducts. However, in several cases control experiments were carried out with only 1 equiv of alkene, with no loss in yield or observable formation of diadducts.

Formation of the *E*-alkenes was favored as exemplified by the reaction of 1-pentene and 2-ethyl-1-butene affording the *E*-adducts 1 and 6 with *E*/*Z* 11:1 and 2:1, respectively. Similarly, (*E*)-3-hexene and (*E*)-4-octene afforded only the *E* adducts 7 and 8, respectively. In the case of the cyclic adducts 3 and 4 it was essential to work up the reactions immediately after quenching in order to prevent further hydrochlorination of the alkene.

In order to preserve the double bond functionality in the hydrazine adducts N–N bond cleavage was effected using lithium in liquid ammonia. As reported by Denmark *et al.*,[11] lithium in liquid ammonia was found to give better yields in this reduction than sodium in ammonia.

1-Methylcyclohexene was found to yield an ene adduct, as evidenced by the mass spectrum of the crude product. However, the product appears to be a mixture of isomers that we have been unable to separate. Furthermore, for some inexplicable reason, the lithium–ammonia reduction fails in this case. Further explorations of unsymmetrical alkenes that can yield more than one product are underway.

In summary, a useful method to effect allylic amination has been developed making use of the efficient ene reaction of DEAD with alkenes catalyzed by $SnCl_4$. Cleavage of resultant diacyl hydrazines to the corresponding carbamates can usually be effected with lithium in liquid ammonia. So far, the method has only been demonstrated with alkenes that can form only one regioisomer, and its scope may be limited to these cases.

Experimental Section

General Details. Chemicals and reagents were purchased from the Aldrich Chemical Co. and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, in $CDCl_3$ solution. Flash chromatography was performed using Merck Kieselgel 60 (230–400 mesh) with the indicated solvents. Analytical TLC was performed using precoated silica gel plates (Merck Kieselgel 60 F_{254}). THF was distilled from sodium benzophenone ketyl before use.

Typical Procedure for the Ene Reaction of Alkenes with DEAD. Preparation of Diethyl (*E*)-1-(2-Penten-1-yl)-1,2-hydrazinedicarboxylate (1). To a solution of DEAD (620 mg, 3.56 mmol) and 1-pentene (0.78 mL, 7.12 mmol) in CH_2Cl_2 (25 mL) cooled to −60 °C under N_2 was added $SnCl_4$ (0.41 mL, 3.56 mmol). After 5 min the yellow solution turned colorless and water (15 mL) was added. After extraction with CH_2Cl_2 (3 × 50 mL) the combined extracts were dried (Na_2SO_4) and concentrated *in vacuo* to afford an oil that was purified by flash chromatography (hexane–EtOAc, 2:1) to afford 760 mg (87%) of the ene adduct 1 as a colorless oil: ^1H NMR δ 0.97 (t, *J* = 7.3 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 6 H), 1.99 (quintet, *J* = 7.3 Hz, 2 H), 3.99 (br m, 2 H), 4.06–4.15 (m, 4 H), 5.39 (dt, *J* = 15.2, 7.1 Hz, 1 H), 5.61 (dt, *J* = 15.2, 7.3 Hz, 1 H), 6.74 (br s, 1 H) which is in agreement with the literature.[7b]

Diethyl 1-(3-Methyl-2-buten-1-yl)-1,2-hydrazinedicarboxylate (2). Prepared from DEAD (1 g, 5.74 mmol), 3-methyl-1-butene (805 mg, 11.48 mmol), and $SnCl_4$ (0.66 mL, 5.74 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 1.27 g (91%) of the ene adduct 2 as a colorless oil: ^1H NMR δ 1.24, 1.25 (2 × t, *J* = 7.1 Hz, 6 H), 1.63 (s, 3 H), 1.71 (s, 3 H), 4.09 (br m, 2 H), 4.16 (t, *J* = 7.1 Hz, 4 H), 5.20 (t, *J* = 7.1 Hz, 1 H), 6.55 (br s, 1 H) which is in agreement with the literature.[7b]

Diethyl 1-(2-Cyclopenten-1-yl)-1,2-hydrazinedicarboxylate (3). Prepared from DEAD (0.62 g, 3.56 mmol), cyclopentene (0.63 mL, 7.12 mmol), and $SnCl_4$ (0.41 mL, 3.56 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 729 mg (85%) of the ene adduct 3 as a colorless oil: IR (film) 3260, 1690 cm^{-1}; ^1H NMR δ 1.12, 1.13 (2 × t, *J* = 7.1 Hz, 6 H), 1.58–2.28 (m, 4 H), 4.03 (br m, 4 H), 5.14 (br s, 1 H), 5.52 (m, 1 H), 5.83 (m, 1 H), 6.86 (br s, 1 H); ^{13}C NMR: δ 14.0, 14.1, 26.3, 30.9, 61.4, 61.9, 64.3, 128.0, 135.3, 155.7, 156.7; MS (FAB, NBA) *m*/*z* 243 (M + H, 23), 177 (100). Anal. Calcd for $C_{11}H_{18}N_2O_4$: C, 54.5; H, 7.5; N, 11.6. Found: C, 54.2; H, 7.6; N, 11.5. Ene adduct 3 has been reported previously[7a] but no spectroscopic data were given.

Diethyl 1-(2-Cyclohexen-1-yl)-1,2-hydrazinedicarboxylate (4). Prepared from DEAD (1.04 g, 5.97 mmol), cyclohexene (1.20 mL, 11.85 mmol), and $SnCl_4$ (0.68 mL, 5.97 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 1.19 g (77%) of the ene adduct 4 as a colorless oil: IR (film) 3270, 1690 cm^{-1}; ^1H NMR δ 1.22 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.59–2.32 (m, 6 H), 4.17 (m, 4 H), 4.76 (br s, 1 H), 5.58 (m, 1 H), 5.82 (m, 1 H), 6.38 (br s, 1 H); ^{13}C NMR δ 14.2, 14.3, 20.8, 24.3, 26.5, 54.3, 61.3, 61.7, 126.7, 131.1, 156.6, 157.0; MS (FAB, NBA) *m*/*z* 257 (M + H, 39), 177 (100). Anal. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.2; H, 7.9; N, 10.9. Found: C, 55.8; H, 7.9; N, 10.6. Ene adduct 4 has been reported previously[7a] but no spectroscopic data were given.

Diethyl 1-(2-Methyl-2-propen-1-yl)-1,2-hydrazinedicarboxylate (5). Prepared from DEAD (1.0 g, 5.74 mmol), isobutylene (644 mg, 11.48 mmol), and $SnCl_4$ (0.66 mL, 5.74 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 1.13 g (86%) of the ene adduct 5 as a colorless oil: ^1H NMR δ 1.24 (t, *J* = 7.1 Hz, 6 H), 1.71 (s, 3 H), 4.04 (s, 2 H), 4.17 (m, 4 H), 4.80 (s, 1 H), 4.87 (s, 1 H), 6.55 (br s, 1 H) which is in agreement with the literature.[7b]

Diethyl 1-(2-Ethyl-2-buten-1-yl)-1,2-hydrazinedicarboxylate (6). Prepared from DEAD (0.62 g, 3.56 mmol), 2-ethyl-1-butene (0.87 mL, 7.12 mmol), and $SnCl_4$ (0.41 mL, 3.56 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 773 mg (84%) of the ene adduct 6 (*E*/*Z*, 2:1) as a colorless oil: IR (film) 3280, 1700 cm^{-1}; ^1H NMR δ 0.97 (t, *J* = 7.4 Hz, 3 H), 1.24 (t, *J* = 7.1 Hz, 6 H), 1.59 (d, *J* = 6.7 Hz, 3 H), 1.97 (q, *J* = 7.4 Hz, 2 H), 4.02 (s, 2 H), 4.16 (m, 4 H), 5.29 (q, *J* = 6.7 Hz, 1H), 5.46 (q, *J* = 6.7 Hz, 1H), 5.81 (br s), 6.46 (br s). MS (FAB, NBA) *m*/*z* 259 (M + H, 100), 177 (57). Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.8; H, 8.6; N, 10.8. Found: C, 55.8; H, 8.5; N, 11.1.

Diethyl (*E*)-1-(2-Hexen-4-yl)-1,2-hydrazinedicarboxylate (7). Prepared from DEAD (0.52 g, 2.97 mmol), (*E*)-3-hexene (0.50 g, 5.94 mmol), and $SnCl_4$ (0.34 mL, 2.97 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 727 mg (95%) of the ene adduct 7 as a colorless oil: IR (film) 3290, 1700 cm^{-1}; H NMR δ 0.95 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.0 Hz, 3 H), 1.16 (t, *J* = 7.0 Hz, 3 H), 1.39–1.44 (m, 2 H), 1.59 (d, *J* = 6.3 Hz, 3 H), 4.07 (m, 4 H), 4.34 (m, 1 H), 5.32 (dd, *J* = 15.0, 7.0 Hz, 1 H), 5.53 (dq, *J* = 15.0, 7.2 Hz, 1 H), 6.61 (br s, 1 H); ^{13}C NMR δ 10.6, 14.2, 14.3, 17.6, 24.7, 61.5, 61.5, 61.9, 128.1, 128.8, 156.0, 156.1; MS (FAB, NBA) *m*/*z* 259 (M + H, 26), 177 (100). Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.8; H, 8.6; N, 10.8. Found: C, 55.3; H, 8.6; N, 10.8.

Diethyl (*E*)-1-(3-Octen-5-yl)-1,2-hydrazinedicarboxylate (8). Prepared from DEAD (0.62 g, 3.56 mmol), (*E*)-4-octene (1.12 mL, 7.12 mmol), and $SnCl_4$ (0.41 mL, 3.56 mmol). Purification by flash chromatography (hexane–EtOAc, 4:1) afforded 816 mg (80%) of the ene adduct 8 as a colorless oil: IR (film) 3270, 1700 cm^{-1}; ^1H NMR δ 0.89 (t, *J* = 7.2 Hz, 3 H), 0.95 (t, *J* = 7.4 Hz, 3 H), 1.24 (m, 6 H), 1.27–1.65 (m, 4 H), 2.01 (quintet, *J* = 7.4 Hz, 2 H), 4.16 (m, 4 H), 4.53 (m, 1 H), 5.36 (dd, *J* = 15.4, 7.1 Hz, 1 H), 5.64 (dt, *J* = 15.4, 7.4 Hz, 1 H), 6.20 (br s, 1 H); ^{13}C NMR: δ 13.3–14.4, 19.0, 25.2, 33.7, 59.5, 61.5, 61.6, 126.6, 134.9, 155.9, 156.4; MS (FAB, NBA) *m*/*z* 287 (M + H, 11), 177 (100). Anal. Calcd for $C_{14}H_{26}N_2O_4$: C, 58.7; H, 9.2; N, 9.8. Found: C, 58.5; H, 9.1; N, 9.9.

Typical Procedure for the Conversion of Ene Adducts to Carbamates. Preparation of (*E*)-*N*-(Ethoxycarbonyl)-1-amino-2-pentene (9). To 15 mL of anhydrous liquid NH_3 cooled to −78 °C was added a solution of 1 (400 mg, 1.64 mmol) in dry

(11) Denmark, S. E.; Nicaise, O.; Edwards, J. P. *J. Org. Chem.* **1990**, *55*, 6219.

THF (5 mL). Freshly-cut lithium metal (54 mg, 7.88 mmol, 4.8 equiv) was added to the solution and a permanent blue color developed. The cold bath was removed and the reaction mixture stirred for 1 h at reflux (−33 °C). The reaction was quenched by the addition of solid NH_4Cl (878 mg, 16.4 mmol, 10.0 equiv) and the NH_3 allowed to evaporate. The residue was dissolved in water (5 mL) and extracted with Et_2O (3 × 50 mL). The ethereal extracts were dried (Na_2SO_4) and concentrated *in vacuo* to afford an oil that was purified by flash chromatography (hexane–Et_2O, 4:1) to afford 221 mg (86%) of **9** as a colorless oil. IR (film) 3320, 1700 cm^{-1}; ^1H NMR δ 0.96 (t, J = 7.4 Hz, 3 H), 1.22 (t, J = 7.0 Hz, 3 H), 2.02 (m, 2 H), 3.72 (m, 2 H), 4.10 (q, J = 7.0 Hz, 2H), 4.63 (br s, 1 H), 5.43 (dt, J = 15.4, 6.3 Hz, 1 H), 5.63 (dt, J = 15.4, 6.2 Hz, 1 H); ^{13}C NMR δ 13.4, 14.6, 25.1, 42.9, 60.7, 125.1, 134.8, 156.5. MS (EI) m/z 157 (M^+, 14), 128 (100). Anal. Calcd for $C_8H_{15}NO_2$: C, 61.1; H, 9.6; N, 8.9. Found: C, 60.9; H, 9.7; N, 9.0.

***N*-(Ethoxycarbonyl)-1-amino-3-methyl-2-butene (10).** Prepared from **2** (300 mg, 1.23 mmol) and lithium metal (43 mg, 6.19 mmol, 5.0 equiv). Purification by flash chromatography (hexane–Et_2O, 4:1) afforded 139 mg (72%) of **10** as a colorless oil: IR (film) 3310, 1680 cm^{-1}; ^1H NMR δ 1.23 (t, J = 7.3 Hz, 3 H, OCH_2CH_3), 1.61 (s, 3 H, Me), 1.72 (s, 3 H, Me), 3.73 (m, 2 H, CH_2N), 4.13 (m, 2 H, OCH_2), 4.57 (br s, 1 H, NH), 5.18 (t, J = 7.0 Hz, 1 H, 2-H); ^{13}C NMR δ 14.5, 17.6, 25.5 (q, 3 × CH_3), 53.3 (t, C-1), 60.6 (t, OCH_2), 120.5 (d, C-2), 135.8 (s, C-3), 156.5 (s, C=O). Anal. Calcd for $C_8H_{15}NO_2$: C, 61.1; H, 9.6; N, 8.9. Found: C, 61.4; H, 9.8; N, 9.0.

***N*-(Ethoxycarbonyl)-1-amino-2-cyclopentene (11).** Prepared from **3** (500 mg, 2.07 mmol) and lithium metal (69 mg, 9.94 mmol, 4.8 equiv). Purification by flash chromatography (hexane–Et_2O, 4:1) afforded 239 mg (74%) of **11** as a colorless oil: IR (film) 3310, 1690 cm^{-1}; ^1H NMR δ 1.20 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.53–2.39 (m, 4 H), 4.08 (m, 2 H, OCH2), 4.63 (br m, 1 H, CHN), 4.73 (br s, 1 H, NH), 5.66 (m, 1 H, 2-H), 5.89 (m, 1 H, 3-H); ^{13}C NMR δ 14.5, 30.9, 31.5, 57.0, 60.5, 131.2, 134.2, 155.9; MS (EI) m/z 155 (M^+, 24) 126 (87), 82 (100). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.9; H, 8.4; N, 9.0. Found: C, 61.8; H, 8.5; N, 9.2.

***N*-(Ethoxycarbonyl)-1-amino-2-cyclohexene (12).** Prepared from **4** (500 mg, 1.95 mmol) and lithium metal (68 mg, 9.75 mmol, 5.0 equiv). Purfication by flash chromatography (hexane–Et_2O, 4:1) afforded 237 mg (72%) of **12** as a colorless oil: IR (film) 3300, 1690 cm^{-1}; ^1H NMR δ 1.15 (t, J = 7.1 Hz, 3 H), 1.18–1.94 (m, 6 H), 4.01 (m, 2 H), 4.11 (m, 1 H), 4.79 (br s, 1 H), 5.52 (dd, J = 10.0, 2.8 Hz, 1 H), 5.73 (m, 1 H); ^{13}C NMR δ 14.4, 19.5, 24.6, 29.6, 45.9, 60.4, 127.8, 130.3, 155.8. Anal. Calcd for $C_9H_{15}NO_2$: C, 63.9; H, 8.9; N, 8.3. Found: C, 63.6; H, 9.0; N, 8.3.

***N*-(Ethoxycarbonyl)-1-amino-2-ethyl-2-butene (14).** Prepared from **6** (200 mg, 0.78 mmol) and lithium metal (27 mg, 3.9 mmol, 5.0 equiv). Purification by flash chromatography (hexane–Et_2O, 4:1) afforded 79 mg (67%) of **14** (*E*/*Z*, 2:1) as a colorless oil: IR (film) 3310, 1700 cm^{-1}; ^1H NMR δ 0.93 (t, J = 7.4 Hz, 3 H), 1.12–1.19 (m, 3 H), 1.54 (d, J = 6.6 Hz, 3H), 1.59 (d, J = 6.6 Hz, 3H), 2.09–2.18 (m, 2 H), 3.39 (s, 1H), 3.42 (s, 1H), 4.06 (m, 2 H), 4.44 (br s 1 H), 4.53 (br s, 1H) 5.27–5.32 (m, 1 H); MS (EI) m/z 171 (M^+, 66), 142 (100). Anal. Calcd for $C_9H_{17}NO_2$: C, 63.1; H, 10.0; N, 8.2. Found: C, 62.9; H, 9.7; N, 7.8.

***(E)*-*N*-(Ethoxycarbonyl)-4-amino-2-hexene (15).** Prepared from **7** (500 mg, 1.94 mmol) and lithium metal (67 mg, 9.69 mmol, 5.0 equiv). Purification by flash chromatography (hexane–Et_2O, 4:1) afforded 252 mg (76%) of **15** as a colorless oil: IR (film) 3310, 1700 cm^{-1}; ^1H NMR δ 0.88 (t, J = 7.4 Hz, 3 H), 1.22 (t, J = 7.1 Hz, 3 H), 1.49 (quintet, J = 7.4 Hz, 2 H), 1.65 (d, J = 6.3 Hz, 3 H), 3.97 (m, 1 H), 4.08 (q, J = 7.4 Hz, 2 H), 4.56 (br s, 1 H), 5.30–5.35 (m, 1 H, 5.54–5.61 (m, 1 H); ^{13}C NMR δ 10.6, 14.5, 17.6, 28.4, 53.4, 60.5, 126.2, 131.5, 156.0. Anal. Calcd for $C_9H_{17}NO_2$: C, 63.1; H, 10.0; N, 8.2. Found: C, 62.8; H, 9.9; N, 8.1.

***(E)*-*N*-(Ethoxycarbonyl)-5-amino-3-octene (16).** Prepared from **8** (500 mg, 1.75 mmol) and lithium metal (60 mg, 8.70 mmol, 5.0 equiv). Purification by flash chromatography (hexane–Et_2O, 4:1) afforded 247 mg (71%) of **16** as a colorless oil: IR (film) 3310, 1700 cm^{-1}; ^1H NMR δ 0.89 (t, J = 7.4 Hz, 3 H), 0.95 (t, J = 7.4 Hz, 3 H), 1.22 (t, J = 7.1 Hz, 3 H), 1.29–1.46 (m, 4 H), 2.01 (quintet, J = 7.4 Hz, 2 H), 4.06–4.10 (m, 3 H), 4.51 (br s, 1 H), 5.28 (dd, J = 15.3, 6.2 Hz, 1 H), 5.61 (dt, J = 15.3, 7.4 Hz, 1 H); ^{13}C NMR δ 13.4, 13.7, 14.5, 18.8, 25.1, 37.8, 53.3, 60.5, 129.4, 132.7, 156.1; MS (EI) m/z 199 (M^+, 8), 170 (55), 156 (100). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.3; H, 10.6; N, 7.0. Found: C, 65.8, H, 10.6; N, 7.3.

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