$CHCl_3/CH_3OH$ (8:1, v/v) or $CHCl_3$/acetone/CH_3OH (16:3:1, v/v/v) as developing solvents.

(−)-Xanthobilirubic Acid (*R*)-α-Methylbenzylamide (1). Xanthobilirubic acid[12] (181 mg, 0.6 mmol) was dissolved in 50 mL of dry, distilled *N,N*-dimethylformamide. To this solution were added diphenylphosphoryl azide (0.826 g, 3 mmol), triethylamine (160 mg, 1.6 mmol), and (*R*)-(+)-α-methylbenzylamine (160 mg, 1.6 mmol), and (*R*)-(+)-α-methylbenzylamine (145 mg, 1.2 mmol), and the solution was heated for 6–12 h under N_2 at 55–60 °C until the xanthobilirubic acid was consumed (as checked by TLC). After the solution was cooled to room temperature, the solvent was removed at reduced pressure (rotovap) to afford a yellow solid. The latter was stirred in 20 mL of ethyl acetate for 30 min and then filtered to afford 210 mg (86%) of yellow crystals that gave one major spot on TLC. Recrystallization from dimethylformamide/1-butanol gave 101 mg (42%) of an analytical sample: mp 307–309 °C (sealed capillary); $[\alpha]^{25}_{589}$ −60.3° (*c* 0.83); IR (KBr) ν 3350, 2980, 2930, 2880, 1670, 1640, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (3 H, t, *J* = 7.5 Hz), 1.39 (3 H, d, *J* = 7 Hz), 1.91 (3 H, s), 2.08 (3 H, s), 2.30 (3 H, s), 2.5–2.7 (6 H, m), 4.8–5.1 (1 H, m), 6.10 (1 H, m), 7.0–7.5 (5 H, m), 10.13 (1 H, s), 11.00 (1 H, s); ^1H NMR (DMSO-d_6) δ 1.04 (3 H, t, *J* = 7 Hz), 1.26 (3 H, d, *J* = 7 Hz), 1.72 (3 H, s), 1.96 (3 H, s), 2.07 (3 H, s), 2.15–2.35 (6 H, m), 4.84 (1 H, q, *J* = 7 Hz), 5.89 (1 H, s), 7.0–7.4 (5 H, m), 9.70 (1 H, s), 10.22 (1 H, s); UV ϵ^{405}_{max} = 33 800 ($CHCl_3$), ϵ^{414}_{max} = 32 200 (DMSO); CD $\Delta\epsilon^{402}_{max}$ = −3.1, $\Delta\epsilon^{446}$ = 0, $\Delta\epsilon^{446}_{max}$ = +1.3 (4.4 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = −1.3 (3.8 × 10^{-5} M in DMSO). Anal. Calcd for $C_{15}H_{31}N_3O_2$ (405.52): C, 74.04; H, 7.71; N, 10.36. Found: C, 73.84; H, 7.88; N, 10.26.

(+)-Xanthobilirubic Acid (*S*)-α-Methylbenzylamide (2). This enantiomer was prepared as above, in 88% yield (61% recrystallized), with (*S*)-(−)-α-methylbenzylamine. It had the same melting point and spectral data as above, except $[\alpha]^{25}_{589}$ +60.7° (*c* 0.36) and CD $\Delta\epsilon^{402}_{max}$ = +3.1, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{446}_{max}$ = −1.3 (4.4 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = +1.3 (3.6 × 10^{-5} M in DMSO).

(±)-Xanthobilirubic Acid (*R,S*)-α-Methylbenzylamide (5). The racemic mixture was prepared as above, in 82% yield, with racemic α-methylbenzylamine. It had mp 298–299 °C (sealed capillary) and the same spectral properties as above except $[\alpha]_{589}$ 0° and $\Delta\epsilon$ = 0 (in $CHCl_3$ or DMSO from 320–520 nm).

(−)-Xanthobilirubic Acid (*R*)-1-(1-Naphthyl)ethylamide (3). This amide was prepared in 85% yield (55% recrystallized) as above with (*R*)-(+)-1-(1-naphthyl)ethylamine: mp 308–309 °C (sealed capillary); $[\alpha]^{25}_{589}$ −109.2° (*c* 0.36); IR (KBr) ν 3350, 3970, 2920, 2870, 1665, 1635, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (3 H, t, *J* = 7 Hz), 1.56 (3 H, d, *J* = 8 Hz), 1.88 (3 H, s), 2.06 (3 H, s), 2.24 (3 H, s), 2.25–2.75 (6 H, m), 5.5–5.8 (1 H, m), 6.06 (1 H, s), 7.0–7.5 (7 H, m), 10.01 (1 H, s), 10.87 (1 H, s); ^1H NMR (DMSO-d_6) δ 1.08 (3 H, t, *J* = 7 Hz), 1.43 (3 H, t, *J* = 7 Hz), 1.77 (3 H, s), 1.99 (3 H, s), 2.09 (3 H, s), 2.1–2.4 (6 H, m), 4.65 (1 H, q, *J* = 7 Hz), 5.92 (1 H, s), 7.3–8.1 (7 H, m), 9.74 (1 H, s), 10.24 (1 H, s); UV ϵ^{405}_{max} = 32 300 ($CHCl_3$), ϵ^{413}_{max} = 31 900 (DMSO); CD $\Delta\epsilon^{404}_{max}$ = −5.2, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{447}_{max}$ = +2.0 (5.0 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = −1.7 (3.8 × 10^{-5} M in DMSO). Anal. Calcd for $C_{29}H_{33}N_3O_2$ (455.57): C, 76.45; H, 7.30; N, 9.22. Found: C, 76.15; H, 7.50; N, 9.20.

(+)-Xanthobilirubic Acid (*R*)-1-(1-Naphthyl)ethylamide (4). This enantiomeric amide was prepared as above in 80% yield (51% recrystallized) with *S*-(−)-1-(1-naphthyl)ethylamine. It had the same melting point and spectral data as above, except $[\alpha]^{25}_{589}$ +101.2° (*c* 0.33) and CD $\Delta\epsilon^{403}_{max}$ = +5.2, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{447}_{max}$ = −2.0 (4.9 × 10^{-5} M in $CHCl_3$); $\Delta\epsilon^{412}_{max}$ = +1.7 (4.1 × 10^{-5} M in DMSO).

(±)-Xanthobilirubic Acid (*R,S*)-1-(1-Naphthyl)ethylamide (6). The racemic amide was prepared as above in 86% yield from racemic 1-(1-naphthyl)ethylamine. It had mp 289–290 °C (sealed capillary) and the same spectral properties as above, except $[\alpha]_{589}$ 0° and $\Delta\epsilon$ (in $CHCl_3$ or DMSO from 320–520 nm).

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Photochemical Heterocyclization of Functionalized Dienamines

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A series of functionalized dienamines were prepared by base-catalyzed isomerization of *N*-vinylaziridines. Photochemical cyclization of these N-unsubstituted dienamines yielded predominantly pyrroline or pyrrole derivatives.

Photochemical reactions of aryl vinyl heteroatom systems have been studied extensively[1-9] and are often a convenient route to condensed heterocyclic compounds.[10,11] In most of the heterosystems that have been investigated,

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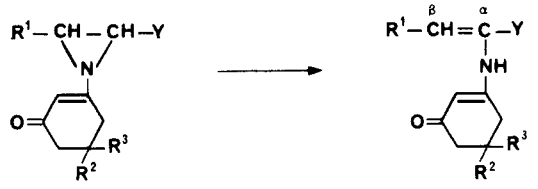
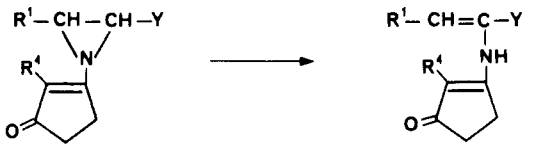
Scheme I



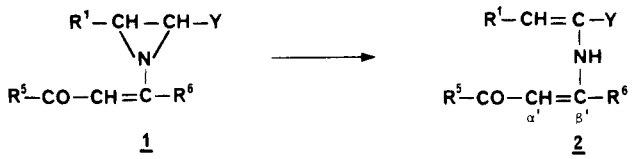
1 2

a $R^1 = R^2 = R^3 = H$; $Y = COOCH(CH_3)_2$
b $R^1 = H$; $R^2 = R^3 = CH_3$; $Y = COOCH(CH_3)_2$
c $R^1 = CH_3$; $R^2 = R^3 = H$; $Y = COOC_2H_5$
d $R^1 = R^2 = R^3 = CH_3$; $Y = COOC_2H_5$
e $R^1 = CH_3$; $R^2 = R^3 = H$; $Y = CN$
f $R^1 = R^2 = R^3 = CH_3$; $Y = CN$



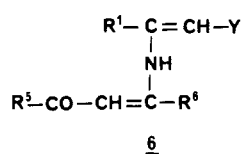
1 2

g $R^1 = R^4 = H$; $Y = COOCH(CH_3)_2$
h $R^1 = CH_3$; $R^4 = H$; $Y = COOC_2H_5$
i $R^1 = H$; $R^4 = CH_3$; $Y = COOCH(CH_3)_2$
j $R^1 = R^4 = CH_3$; $Y = COOC_2H_5$



1 2

k $R^1 = R^6 = H$; $R^5 = OC_2H_5$; $Y = COOCH(CH_3)_2$
l $R^1 = H$; $R^5 = R^6 = CH_3$; $Y = COOCH(CH_3)_2$
m $R^1 = CH_3$; $R^5 = OC_2H_5$; $R^6 = H$; $Y = COOC_2H_5$
n $R^1 = R^5 = R^6 = CH_3$; $Y = COOC_2H_5$

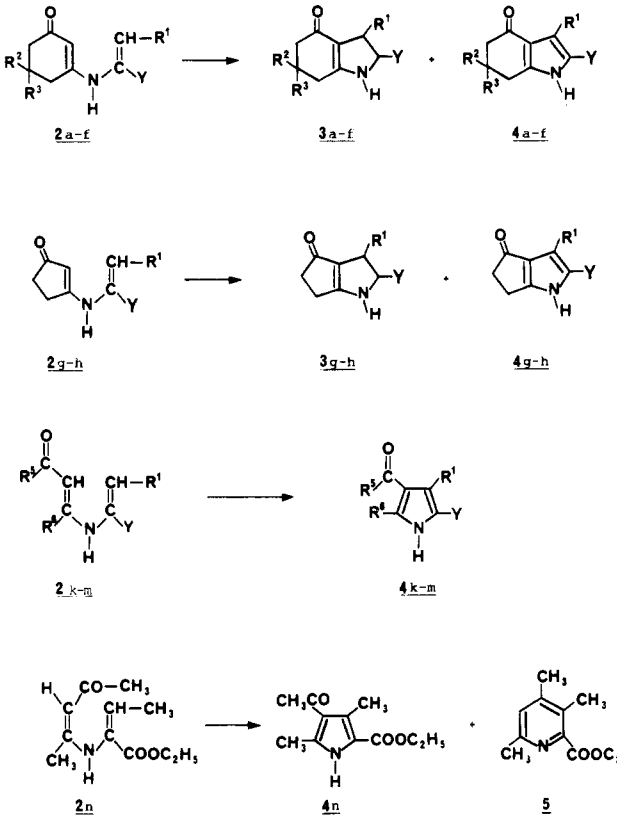


6

o $R^1 = R^5 = R^6 = CH_3$; $Y = CN$

aromatic rings provide at least one active π bond of the diene chromophore. Photoreaction of the divinyl compounds containing a heteroatom have received little attention. One study has been concerned with the photolysis of bis(2,2-diphenylvinyl) ether, leading mainly to the cage recombination product of initially formed vinylvinyloxy radical pairs;[12] reported photoreaction of β,β'-diphenyldivinyl sulfide consisted of cyclization to *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane[13] and photocyclization of 1,1-bis(methoxycarbonyl)divinylamine failed.[14]

Scheme II



2a-f 3a-f 4a-f

2g-h 3g-h 4g-h

2k-m 4k-m

2n 4n 5

Recently we reported the base-catalyzed isomerization of *N*-vinylaziridines to α,β-dehydro-α-enanimo acid derivatives.[15] These compounds are isoelectronic with the pentadienyl anion. This fact and the absence of an investigation on the photochemistry of the divinylamines prompted us to study the photochemical reactions of these α,β-dehydro-α-enamino acid derivatives. In this paper we report on the photocyclization of these derivatives and we show that these compounds, which lack N-substitution, can be precursors of pyrroline and pyrrole derivatives.

Results

The synthesis of dienamines **2a–o** follows the previously reported procedure[15] (Scheme I) and is outlined in the Experimental Section.

A degassed ethereal solution of the dienamine **2a** was irradiated under argon with quartz-filtered light and the product was purified by column chromatography. The major product from the reaction was obtained in 35% isolated yield and was identified as the hexahydroindolone **3a**. The minor compound (19% isolated yield) was assigned the tetrahydroindolone structure **4a**. Irradiation of compounds **2b,c,g,h** also resulted in isolation of pyrroline **3b,c,g,h** and pyrrole **4b,c,g,h** derivatives (Scheme II). Photocyclization of **2c,h** was conducted on a mixture of the *Z* and *E* isomers in a *E*/*Z* ratio of 55:45 and 50:50, respectively. It occurred to give **3c,h** as a mixture of di-

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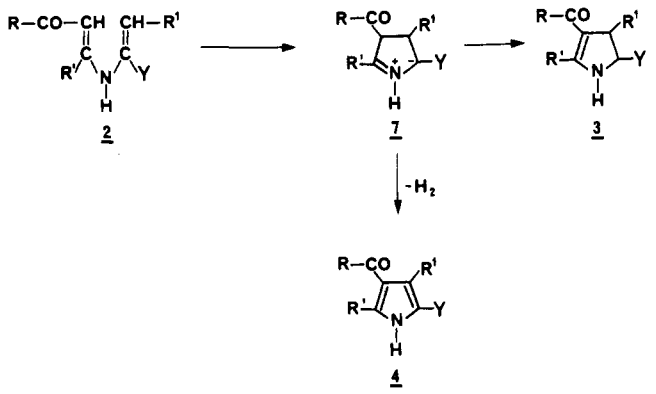
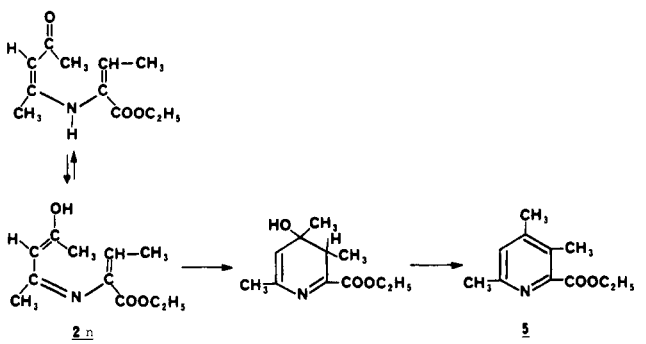
Scheme III



Scheme IV



astereoisomers in a trans/cis ratio of 55:45 and 50:50, respectively, which were separated by silica gel chromatography. Similar results in the photocyclization of **2c** were obtained by using other solvents such as THF or CH_3CN; with C_6H_6 or *i*-PrOH, the reaction did not seem to go to completion, there was always a little **2c** left, and with MeOH the reaction was slower. Pyrex-filtered or quartz-filtered irradiation of **2h** led to the same results.

Irradiation under nitrogen or argon of degassed ether solutions of compounds **2d–f,k–m** afforded only the corresponding pyrrole derivatives **4d–f,k–m**. Prior to photocyclization of **2k** photoisomerization about the α',β'-olefinic bond occurred, irradiation of the *Z* isomer leading to the *E* derivative.

Irradiation of **2n** in ether gave substituted pyrrole **4n** as the main product accompanied by small amounts of a compound which was assigned structure **5** (Scheme II).

Irradiation of methyl-substituted **2i,j** under the same experimental conditions gave mainly polymerization.

β-Enamino compounds **6e,l** were prepared as minor compounds in the base-catalyzed isomerization of *N*-vinylaziridines **1e,l**; **6o** was the sole compound obtained by isomerization of *N*-vinylaziridine **1o**. We have not been able to convert these dienamines to the heterocyclic products; photoisomerization of the α,β-olefinic bond occurred on irradiation of **6l**; no photoreaction was observed with derivatives **6e,o**.

Structural and stereochemical assignments were made on the basis of physical and spectral data (see Experimental section).

Discussion

A probable mechanism[1h,5j] for photocyclization of dienamines **2** involves a conrotatory electrocyclic process which generates intermediate ylides **7** (Scheme III) from which a suprafacial [1,4] hydrogen migration gives the pyrroline derivatives **3**. In this stereospecific process, the relative stereochemistry of C-2 and C-3 in the cyclic compounds **3** is dictated by the geometry of the olefins **2**. Thus the *E*-olefins (**2c** or **2h**) are expected to produce cyclic products **3** with a trans relationship between the C-2 and C-3 substituents, while a cis stereochemistry results from the *Z*-olefins. The observation of a 55:45 trans/cis product ratio from **2c** (*E*/*Z* 50:50) constitutes evidence for the concerted nature of the reaction. It also rules out a photochemical *Z*–*E* isomerization of olefins **2c** and **2h** prior to the cyclization.

Pyrrole derivatives **4** may be formed from azomethine ylides **7** by direct aromatization via deprotonation. Alternatively, azomethine ylides **7** may rearrange to pyrrolines **3** which may oxidize to pyrroles **4**. Control experiments indicated that pyrroline derivative **3g** was not converted to pyrrole **4g** under the conditions of the experiment. This result rules out the intermediate of **3** in the formation of **4**.

An alternative procedure provides a rationalization for the formation of **5**: the *Z*-enamino ketone **2n** may react in its tautomeric imino–enol form to give an intermediate from which pyridine **5** derives by the loss of water (Scheme IV).

Photocyclization of **2i,j** would have produced **3i,j** via azomethine ylide **7** and 1,4-methyl migration, but these products were not detected in photoreaction of **2i,j**.

Our photochemical studies show that cyclization is possible with compounds **2** which possess an electron-withdrawing substituent Y cross-conjugated with the heteroatom and that it is not possible with compounds **6** where the Y group is in a β-position from the heteroatom. We think that the cross-conjugated Y group provides a stabilization of the intermediate ylide.

Our results show that N-unsubstituted pyrroline and pyrrole derivatives can be prepared by photoheterocyclization of dienamines which lack N-substitution. A few reports in the literature are concerned with photocyclization of aryl enamino compounds of this type.[4,5f,i]

The compounds described are of potential value because of the presence of these nitrogen-containing heterocycles in natural products and pharmaceutical agents. For example 4-oxo-4,5,6,7-tetrahydroindole derivatives are used in the synthesis of indoles bearing functionalities at the 4-position, which are of great importance because of their wide variety of biological activities;[16,17] pyrrole derivatives are also used in the synthesis of porphyrins.[18]

Experimental Section

Infrared spectra were measured in liquid films or in solution on a Perkin-Elmer 157 spectrometer. UV spectra were obtained on a Beckman DU-8 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded at 60 MHz (Perkin-Elmer R-24 or JEOL 60 for ^1H, JEOL FX60 for ^{13}C) in $CDCl_3$ solution. Chemical shifts (δ) are given in ppm relative to internal TMS. Mass spectra were obtained from Service Central d'Analyse of CNRS in Lyon-Solaize. Photochemical experiments were carried out with a 450-W Hanovia high pressure mercury vapor lamp in a quartz immersion well. Column chromatography was conducted with Merck silica gel 7734 and hexane–ethyl acetate as eluent.

Preparation of *N*-Vinylaziridines 1. The *N*-vinylaziridines **1a–o** were prepared through the reaction of secondary aziridines with acetylenic compounds or activated vinylic chlorides, according to the method in the literature.[15]

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Compounds **1d** and **1m** have been previously described.[15]

***N*-Vinylaziridine 1a**: 63% yield; mp 64–65 °C; ^{1}H NMR δ 1.25 (d, 6 H, J = 7 Hz), 1.80–2.60 (m, 8 H), 2.80 (dd, 1 H, J = 3.0 Hz, J = 5.8 Hz), 5.08 (septet, 1 H, J = 7 Hz), 5.50 (s, 1 H); ^{13}C NMR δ 21.7, 21.9, 28.6, 32.4, 36.2, 37.0, 69.5, 112.6, 168.1, 170.4, 198.8. Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28; O, 21.52. Found: C, 64.30; H, 7.52; N, 6.35; O, 21.51.

***N*-Vinylaziridine 1b**: 44% yield; ^{1}H NMR δ 1.10 (s, 6 H), 1.31 (d, 6 H, J = 7 Hz), 2.20 (s, 2 H), 2.37 (s, 2 H), 2.15–2.30 (m, 1 H), 2.58 (dd, 1 H, J = 1.8 Hz, J = 3.0 Hz), 2.75 (dd, 1 H, J = 3.0 Hz, J = 5.8 Hz), 5.10 (septet, 1 H, J = 7 Hz), 5.58 (s, 1 H); ^{13}C NMR δ 21.7, 28.2, 32.3, 33.2, 36.2, 42.4, 50.9, 69.5, 111.5, 168.0, 168.5, 198.7. Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.93; H, 8.37; N, 5.58. Found: C, 66.49; H, 8.37; N, 5.59.

***N*-Vinylaziridine 1c**. The cis isomer[19] of **1c** was isolated in 82% yield: ^{1}H NMR δ 1.25 (t, 3 H, J = 7 Hz), 1.35 (d, 3 H, J = 7 Hz), 1.70–2.70 (m, 7 H), 2.80 (d, 1 H, J = 6 Hz), 4.25 (q, 2 H, J = 7 Hz), 5.47 (s, 1 H); ^{13}C NMR δ 13.3 (q), 14.3 (q), 21.9 (t), 28.2 (t), 37.0 (t), 40.2 (d), 41.2 (d), 61.5 (t), 112.1 (d), 167.7 (s), 171.1 (s), 199.0 (s). Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.39; H, 7.78; N, 6.09.

***N*-Vinylaziridine 1e**. A mixture of the cis and trans isomers[19] of **1e** was isolated in 53% yield (cis/trans = 75/25): ^{1}H NMR δ 1.38 (d, 0.75 H, J = 5.0 Hz), 1.48 (d, 2.25 H, J = 5.8 Hz), 1.80–2.60 (m, 7 H), 2.79 (d, 0.25 H, J = 4.2 Hz), 2.96 (d, 0.75 H, J = 6 Hz), 5.48 (s, 0.75 H), 5.61 (s, 0.25 H); ^{13}C NMR δ 15.5, 16.0, 21.7, 27.9, 28.1, 28.4, 28.8, 36.8, 39.3, 41.5, 112.7, 113.7, 116.0, 116.2, 167.2, 169.4, 198.7, 198.8. Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.82; N, 15.91. Found: C, 68.43; H, 6.99; N, 15.62.

***N*-Vinylaziridine 1f.** The cis isomer[19] of **1f** was isolated in 42% yield: mp 98–100 °C; IR 2250, 1700, 1620 cm^{-1}; ^{1}H NMR δ 1.0 (s, 6 H), 1.90 (s, 2 H), 2.10 (s, 2 H), 1.50 (d, 3 H, J = 5.5 Hz), 2.30 (d, 1 H, J = 6.0 Hz), 2.0–2.70 (m, 1 H), 5.53 (s, 1 H); ^{13}C NMR δ 15.5, 28.1, 28.8, 33.1, 39.3, 41.8, 50.8, 111.7, 115.9, 167.2, 198.6. Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.59; H, 7.84; N, 13.73. Found: C, 70.88; H, 7.85; N, 13.59.

***N*-Vinylaziridine 1g**: 65% yield; ^{1}H NMR δ 1.80 (d, 6 H, J = 7 Hz), 2.20–2.80 (m, 6 H), 2.90 (dd, 1 H, J = 3.0 Hz, J = 5.5 Hz), 5.12 (septet, 1 H, J = 7 Hz), 5.45 (br s, 1 H); ^{13}C NMR δ 21.6 (q), 28.7 (t), 32.9 (t), 34.9 (t), 36.6 (d), 69.6 (d), 115.2 (d), 167.7 (s), 184.2 (s), 206.7 (s). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70. Found: C, 63.25; H, 7.22; N, 6.53.

***N*-Vinylaziridine 1h.** The cis isomer[19] of **1h** was isolated in 82% yield: mp 70-72°; ^{1}H NMR δ 1.28 (d, 3 H, J = 7 Hz), 1.40 (d, 3 H, J = 6 Hz), 2.30–2.80 (m, 5 H), 2.90 (d, 1 H, J = 5.6 Hz), 4.28 (q, 2 H, J = 7 Hz), 5.56 (t, 1 H, J = 1.2 Hz); ^{13}C NMR δ 13.0, 14.2, 28.3, 34.9, 40.5, 41.8, 61.6, 114.7, 167.4, 184.7, 206.7. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70; O, 22.97. Found: C, 63.07; H, 7.37; N, 6.60; O, 22.87.

***N*-Vinylaziridine 1i**: 46% yield; ^{1}H NMR δ 1.20 (d, 6 H, J = 6 Hz), 1.62 (s, 3 H), 2.0–2.80 (m, 6 H), 2.99 (dd, 1 H, J = 3.2 Hz, J = 5.8 Hz), 5.05 (septet, 1 H); ^{13}C NMR δ 6.8, 21.5, 26.8, 31.8, 33.6, 36.1, 69.4, 123.0, 167.9, 175.7, 206.5. Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.77; H, 7.67; N, 6.31.

***N*-Vinylaziridine 1j.** The cis isomer[19] of **1j** was isolated in 89% yield: ^{1}H NMR δ 1.38 (d, 3 H, J = 7 Hz), 1.41 (d, 3 H, J = 5.8 Hz), 1.70 (br s, 3 H), 2.20–2.50 (m, 4 H), 2.65 (dq, 1 H, J = 5.8 Hz, J = 6 Hz), 2.97 (d, 1 H, J = 6 Hz), 4.28 (q, 2 H, J = 7 Hz); ^{13}C NMR δ 9.2 (q), 15.5 (q), 16.4 (q), 28.8 (t), 35.8 (t), 42.1 (d), 43.5 (d), 63.8 (t), 125.1 (s), 169.9 (s), 178.8 (s), 209.1 (s). Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.26; H, 7.67; N, 6.07.

***N*-Vinylaziridine 1k.** A mixture of the E and Z isomers of **1k** was isolated in 63% yield (E/Z = 60/40): ^{1}H NMR δ 1.25 (d, 6 H, J = 7.0 Hz), 1.20 (t, 3 H, J = 7 Hz), 2.0–2.6 (m, 2 H), 2.73 (dd, 0.6 H, J = 3.0 Hz, J = 6.0 Hz), 2.90 (dd, 0.4 H, J = 3.2 Hz, J = 5.8 Hz), 4.15 (q, 2 H, J = 7 Hz), 5.15 (septet, 1 H, J = 7 Hz), 5.20 (d, 0.4 H, J = 9 Hz), 5.40 (d, 0.6 H, J = 13 Hz), 6.60 (d, 0.4 H, J = 9 Hz), 7.45 (d, 0.6 H, J = 13 Hz); ^{13}C NMR δ 14.2, 21.6, 33.5, 35.7, 36.5, 39.6, 59.5, 59.9, 68.9, 69.3, 104.1, 107.2, 151.9, 154.6, 165.2, 166.8, 168.2, 168.4. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.15; H, 7.49; N, 6.17. Found: C, 58.25; H, 7.54; N, 5.82.

(19) Stereochemical relationship of H-2 and H-3.

***N*-Vinylaziridine 1l.** A mixture of the E and Z isomers of **1l** was isolated in 67% yield (E/Z = 80/20): ^{1}H NMR δ 1.35 (d, 6 H, J = 7 Hz), 1.95 (s, 0.6 H), 2.05 (s, 0.6 H), 2.10 (s, 2.4 H), 2.22 (s, 2.4 H), 1.90–2.60 (m, 2 H), 2.78 (dd, 0.8 H, J = 3.2 Hz, J = 6.8 Hz), 3.0 (dd, 0.2 H, J = 3.2 Hz, J = 6.7 Hz), 5.02 (septet, 1 H, J = 7 Hz), 5.60 (s, 0.2 H), 5.68 (s, 0.8 H); ^{13}C NMR δ 18.8, 21.6, 22.2, 31.0, 31.6, 33.0, 34.5, 36.4, 40.0, 68.8, 69.3, 109.5, 110.3, 159.4, 163.8, 168.3, 168.4, 194.6, 196.9. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.56; H, 8.06; N, 6.64. Found: C, 62.08; H, 8.32; N, 6.53.

***N*-Vinylaziridine 1n.** A mixture of the four isomers of **1n** was obtained in 47% yield in which *cis*-**1n**[19] was the most abundant: ^{1}H NMR δ 1.31 (t, 3 H, J = 7.5 Hz), 1.40 (d, 3 H, J = 6.3 Hz), 2.12 (s, 3 H), 2.25 (s, 3 H), 2–2.60 (m, 1 H), 2.77 (d, 1 H, J = 6.2 Hz), 4.27 (q, 2 H, J = 7.5 Hz), 5.72 (s, 1 H); ^{13}C NMR δ 13.5, 14.3, 18.4, 31.7, 40.4, 41.7, 61.5, 109.9, 164.6, 168.0, 197.3. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.56; H, 8.06; N, 6.63. Found: C, 62.20; H, 8.29; N, 6.61.

***N*-Vinylaziridine 1o.** The four isomers of **1o** were obtained in 47% yield. They were not separated: IR 2200, 1780, 1640 cm^{-1}; ^{1}H NMR δ 1.20–1.60 (m, 6 H), 2.10–2.30 (m, 3 H), 2.40–3.0 (m, 2 H), 5.62 and 5.78 (s, 1 H); ^{13}C NMR 15.6, 15.9, 16.1, 17.1, 18.0, 18.6, 21.3, 21.6, 21.8, 28.3, 29.2, 31.2, 31.4, 31.8, 32.8, 39.4, 41.3, 41.8, 43.8, 110.7, 111.2, 111.4, 116.2, 117.0, 117.7, 118.7, 155.9, 159.0, 160.1, 162.5, 195.2, 195.4, 197.0, 197.3. Anal. Calcd for $C_9H_{12}N_2O$: C, 65.85; H, 7.32; N, 17.07. Found: C, 65.56; H, 7.63; N, 16.82.

Preparation of Dienamines 2 and 6. The dienamines were prepared by the NaI-catalyzed isomerization of *N*-vinylaziridines **1a–o** according to the procedure previously described.[15]

Dienamines **2d** and **2m** have previously been described.[15]

Dienamine 2a: 42% yield; UV max (EtOH) 287 nm (ε 11 440); UV max (Et_2O) 288 nm (ε 11 540); ^{1}H NMR δ 1.30 (d, 6 H, J = 7 Hz), 1.8–2.8 (m, 6 H), 5.18 (septet, 1 H, J = 7 Hz), 5.42 (d, 1 H, J = 1.5 Hz), 5.78 (s, 1 H), 5.98 (d, 1 H, J = 1.5 Hz), 6.80 (br s, 1 H); ^{13}C NMR δ 21.6, 30.3, 36.4, 70.4, 103.6, 107.3, 133.1, 158.9, 163.7, 198.8. Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.36; H, 7.50; N, 6.07.

Dienamine 2b: 45% yield; UV max (EtOH) 284 nm (ε 18 700); UV max (Et_2O) 277 nm (ε 10 380); ^{1}H NMR δ 1.0 (s, 6 H), 1.37 (d, 6 H, J = 7 Hz), 2.18 (s, 2 H), 2.23 (s, 2 H), 5.10 (septet, 1 H, J = 7 Hz), 5.40 (d, 1 H, J = 1.5 Hz), 5.72 (s, 1 H), 5.88 (d, 1 H, J = 1.5 Hz), 6.72 (br s, 1 H); ^{13}C NMR δ 21.6, 28.2, 32.6, 44.1, 50.2, 70.3, 102.5, 107.0, 133.2, 156.9, 163.7, 198.7. Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.93; H, 8.37; N, 5.58. Found: C, 66.69; H, 8.44; N, 5.43.

Dienamine 2c. A mixture of the E and Z isomers of **2c** was isolated in 84% yield (E/Z = 55/45); UV max (EtOH) 294 nm (ε 10 776); ^{1}H NMR δ 1.30 (t, 3 H, J = 7 Hz), 1.8–2.8 (m, 6 H), 1.72 (d, 1.35 H, J = 7.4 Hz), 2.10 (d, 1.65 H, J = 7.6 Hz), 4.20 (q, 1.1 H, J = 7 Hz), 4.22 (q, 0.9 H, J = 7 Hz), 4.90 (s, 0.45 H), 5.20 (s, 0.55 H), 6.20 (q, 0.55 H, J = 7.6 Hz), 6.85 (q, 0.45 H, J = 7.4 Hz), 7.00 (br s, 1 H); ^{13}C NMR δ 14.2, 14.4, 21.9, 28.7, 29.0, 36.5, 61.2, 61.3, 99.1, 99.6, 127.6, 128.5, 136.1, 164.2, 164.4, 164.7, 198.1. Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.31; H, 7.80; N, 6.48.

Dienamines 2e and 6e. Column chromatography gave **2e** as a mixture of both possible geometric isomers [60:40; 46% yield; mp 130–132 °C; UV max (EtOH) 290 nm (ε 15 600); UV max (Et_2O) 298 nm (ε 7370), 274 (10 830); ^{1}H NMR δ (DMSO-d_6) 1.78 (d, 1.8 H, J = 7.2 Hz), 1.95 (d, 1.2 H, J = 7 Hz), 2–2.60 (m, 6 H), 4.95 (s, 0.6 H), 5.08 (s, 0.4 H), 6.45 (q, 0.6 H, J = 7.2 Hz), 6.52 (q, 0.4 H, J = 7 Hz), 8.43 (br s, 0.6 H); 8.63 (br s, 0.4 H); ^{13}C NMR δ 13.8, 15.3, 21.6, 28.2, 28.3, 36.4, 100.2, 100.5, 111.2, 111.8, 113.8, 115.7, 140.0, 141.0, 163.6, 163.9, 198.7. Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.82; N, 15.91. Found: C, 67.94; H, 6.84; N, 15.92] and **6e** [16% yield; ^{1}H NMR δ 2–2.60 (m, 6 H), 2.28 (s, 3 H), 5.02 (s, 1 H), 5.80 (s, 1 H), 8.20 (br s, 1 H). Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.82; N, 15.91. Found: C, 67.87; H, 6.86; N, 15.87].

Dienamines 2f and 6f. ^{1}H NMR analysis of the crude reaction product indicated that **2f** (both possible geometric isomers) and **6f** were present (45:35:20); column chromatography gave **2f** as a mixture of isomers [40% yield; UV max (EtOH) 296 nm (ε 19 248); UV max (Et_2O) 289 nm (ε 16 730), 261 (21 852); ^{1}H NMR δ 1.02 (s, 6 H), 1.80 (d, 1.65 H, J = 7.5 Hz), 2.0 (d, 1.35 H, J = 7.5 Hz), 2.10–2.40 (m, 4 H), 5.15 (s, 0.55 H), 5.30 (s, 0.45 H), 6.40 (q, 1 H, J = 7.5 Hz), 8.0 (br s, 1 H); ^{13}C NMR δ 13.7, 15.2, 28.1, 32.9, 41.7, 50.3, 99.0, 111.3, 111.7, 113.7, 115.7, 139.9, 141.1, 162.0,

198.2. Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.59; H, 7.84; N, 13.73. Found: C, 70.86; H, 7.71; N, 13.60] and **6f** [^{1}H NMR δ 1.05 (s, 6 H), 2.25 (s, 3 H), 2.15–2.50 (m, 4 H), 4.98 (s, 1 H), 5.75 (s, 1 H), 7.80 br s, 1 H)].

Dienamine 2g: 33% yield; mp 112–113 °C; ^{1}H NMR δ 1.30 (d, 6 H, J = 6 Hz), 2.0–3.0 (m, 4 H), 5.15 (septet, 1 H, J = 6 Hz), 5.30 (d, 1 H, J = 1.8 Hz), 5.58 (br s, 1 H), 5.82 (br s, 1 H), 7.40 (br s, 1 H); ^{13}C NMR δ 21.7, 29.6, 32.9, 70.5, 105.2, 105.8, 134.1, 163.5, 169.6, 206.6. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70; O, 22.96. Found: C, 62.86; H, 7.08; N, 6.60; O, 22.87.

Dienamine 2h. A mixture of the E and Z isomers of **2h** was isolated in 74% yield (E/Z = 50/50); UV max (EtOH) 262 nm (ϵ 16 932); ^{1}H NMR δ 1.22 (d, 1.5 H, J = 7.5 Hz), 1.25 (d, 1.5 H, J = 7.2 Hz), 1.75 (d, 1.5 H, J = 7.5 Hz), 2.05 (d, 1.5 H, J = 7.5 Hz), 2.2–2.9 (m, 4 H), 4.18 (q, 1 H, J = 7.5 Hz), 4.23 (q, 1 H, J = 7.2 Hz), 4.80 (s, 0.5 H), 5.15 (s, 0.5 H), 6.25 (q, 0.5 H, J = 7.5 Hz), 6.85 (q, 0.5 H, J = 7.5 Hz), 8.42 (br s, 0.5 H), 8.55 (br s, 0.5 H); ^{13}C NMR δ 14.2, 27.8, 28.5, 33.5, 34.0, 61.5, 101.6, 102.2, 129.1, 129.9, 132.1, 134.8, 164.2, 175.7, 177.0, 205.7, 206.0. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70. Found: C, 63.38; H, 7.41; N, 6.48.

Dienamine 2i: 39% yield; ^{1}H NMR δ 1.35 (d, 6 H, J = 7 Hz), 1.65 (s, 3 H), 2.0–3.0 (m, 4 H), 5.15 (septet, 1 H, J = 7 Hz), 5.32 (br s, 1 H), 5.70 (br s, 1 H), 7.38 (br s, 1 H); ^{13}C NMR δ 6.7, 21.8, 26.8, 33.6, 70.7, 103.0, 114.4, 133.7, 164.0, 167.8, 203.8.

Dienamine 2j. The Z isomer of **2j** was isolated in 80% yield: UV max (EtOH) 272 nm (ϵ 13 376) 211 (3575); ^{1}H NMR δ 1.35 (t, 3 H, J = 7 Hz), 1.65 (s, 3 H), 1.90 (d, 3 H, J = 7 Hz), 2.50 (s, 4 H), 4.23 (q, 2 H, J = 7 Hz), 6.30 (br s, 1 H), 7.02 (q, 1 H, J = 7 Hz); ^{13}C NMR δ 6.6, 14.0, 14.2, 25.4, 32.8, 61.6, 110.3, 129.5, 137.3, 164.7, 173.8, 204.5.

Dienamine 2k. The Z isomer of **2k** was isolated in 31% yield: ^{1}H NMR δ 1.32 (d, 9 H, J = 6.75 Hz), 4.15 (q, 2 H, J = 6.75 Hz), 4.81 (d, 1 H, J = 8.25 Hz), 4.90 (s, 1 H), 5.10 (septet, 1 H, J = 6.75 Hz), 5.32 (s, 1 H), 6.90 (dq, 1 H, J = 8.25 Hz, J = 12.75 Hz), 9.75 (br d, 1 H, J = 12.75 Hz); ^{13}C NMR δ 14.4, 21.7, 59.4, 69.8, 90.5, 95.7, 135.5, 140.7, 162.9, 169.4.

Dienamines 2l and 6l. Three compounds were isolated from the base-catalyzed opening of *N*-vinylaziridine **1l**, in 75% yield. They were separated by column chromatography and identified as one isomer of **2l** and two isomers of **6l**. The configuration of the α',β'-double bond (enone moiety) was not determined. The stereochemistry of the α,β-double bond of **6l** was based on the vicinal proton coupling constant. **2l**: 28% yield; ^{1}H NMR δ 1.28 (d, 6 H, J = 7 Hz), 2.0 (s, 6 H), 5.0 (septet, 1 H, J = 7 Hz), 5.10 (s, 1 H), 5.20 (s, 1 H), 5.75 (s, 1 H), 13.25 (br s, 1 H). (***E***)**-6l**: 7% yield; ^{1}H NMR δ 1.15 (d, 6 H, J = 6 Hz), 1.95 (s, 3 H), 2.0 (s, 3 H), 4.90 (septet, 1 H, J = 6 Hz), 5.20 (s, 1 H), 5.30 (d, 1 H, J = 13 Hz), 7.50 (t, 1 H, J = 13 Hz), 12.2 (d, 1 H, J = 13 Hz); ^{13}C NMR δ 18.6 (q), 22.0 (q), 29.9 (q), 67.2 (d), 100.3 (d), 101.6 (d), 139.7 (d), 154.8 (s), 167.5 (s), 198.7 (s). (***Z***)**-6l**: 40% yield; ^{1}H NMR δ 1.30 (d, 6 H, J = 6.5 Hz), 2.07 (s, 3 H), 2.15 (s, 3 H), 4.98 (d, 1 H, J = 9 Hz), 5.23 (septet, 1 H, J = 6.5 Hz), 5.38 (s, 1 H), 6.98 (dd, 1 H, J = 9 Hz, J = 13 Hz); ^{13}C NMR δ 18.2, 21.9, 29.7, 66.5, 94.7, 102.5, 139.0, 152.0, 167.0, 197.2.

Dienamine 2n. One isomer of **2n** was isolated with 33% yield. Stereochemistry of the C_α=C_β double bond was not determined. Z configuration of $C_{\alpha'}$=$C_{\beta'}$ bond (enone moiety) was determined on the basis of ^{1}H NMR increments defined by Pascual et al.:[20] ^{1}H NMR δ 1.30 (t, 3 H, J = 6.75 Hz), 1.72 (s, 3 H), 1.83 (d, 3 H, J = 7 Hz), 2.02 (s, 3 H), 4.20 (q, 2 H, J = 6.75 Hz), 5.18 (s, 1 H), 6.92 (q, 1 H, J = 7 Hz), 11.92 (br s, 1 H); ^{13}C NMR δ 13.6, 14.2, 19.0, 29.1, 61.3, 97.1, 129.9, 135.8, 162.0, 164.4, 196.4.

Dienamine 6o: 60% yield; IR 3300, 2200, 1750 cm^{-1}; ^{1}H NMR δ 2.10 (s, 3 H), 2.20 (s, 3 H), 2.25 (s, 3 H), 4.95 (s, 1 H), 5.42 (s, 1 H), 12.16 (br s, 1 H); ^{13}C NMR δ 21.4 (q), 21.8 (q), 30.0 (q), 78.6 (d), 104.0 (d), 118.6 (s), 154.6 (s), 155.4 (s), 198.7 (s).

General Photochemical Procedure. Photochemical experiments were carried out with a 450-W Hanovia high pressure mercury vapor lamp placed in a water-cooled quartz immersion well, under a nitrogen or argon atmosphere. Prior to irradiation, the solution was degassed with ultrasonic waves and bubbling of nitrogen or argon for 30 min. After completion of the reaction, the solvent was evaporated and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:1) of ethyl acetate and hexane gave compounds **4**, and further elution with ethyl acetate gave compounds **3**.

Irradiation of 2a. A solution of **2a** (0.4 g, 0.0061 M) in ether (290 mL) was irradiated for 12 min to give **3a** [35% yield; ^{1}H NMR δ 1.25 (d, 6 H, J = 7 Hz), 1.7–2.7 (m, 6 H), 2.8–3.2 (m, 2 H), 4.42 (dd, 1 H, J = 10.8 Hz, J = 8 Hz), 5.08 (septet, 1 H, J = 7 Hz), 6.60 (br s, 1 H); ^{13}C NMR δ 21.6 (q), 22.3 (t), 23.6 (t), 30.0 (t), 35.7 (t), 59.4 (d), 69.1 (d), 107.5 (s), 170.3 (s), 172.2 (s), 192.0 (s)] and **4a** [19% yield; ^{1}H NMR δ 1.35 (d, 6 H, J = 6.3 Hz), 1.8–3.1 (m, 6 H), 5.15 (septet, 1 H, J = 6.3 Hz), 7.15 (d, 1 H, J = 2.1 Hz), 10.8 (br s, 1 H); ^{13}C NMR δ 21.8, 22.7, 23.5, 37.9, 68.5, 112.4, 121.4, 123.9, 147.3, 161.3, 195.1].

Irradiation of 2b. A solution of **2b** (0.75 g, 0.0103 M) in ether (290 mL) was irradiated for 12 min to give **3b** [50% yield; ^{1}H NMR δ 1.05 (s, 6 H), 1.20 (d, 6 H, J = 6 Hz), 2.15 (s, 2 H), 2.25 (s, 2 H), 2.4–3.4 (m, 2 H), 4.40 (dd, 1 H, J = 10.4 Hz, J = 7.6 Hz), 5.0 (septet, 1 H, J = 6 Hz), 6.60 (br s, 1 H); ^{13}C NMR δ 21.6, 28.6, 34.3, 37.4, 50.0, 59.6, 69.3, 106.4, 169.1, 172.2, 191.3] and **4b** [17% yield; mp 158–160 °C; ^{1}H NMR δ 1.10 (s, 6 H), 1.35 (d, 6 H, J = 6 Hz), 2.39 (s, 2 H), 2.75 (s, 2 H), 5.15 (septet, 1 H, J = 6 Hz), 7.18 (d, 1 H, J = 1.5 Hz), 10.75 (br s, 1 H); ^{13}C NMR δ 21.9 (q), 28.5 (q), 35.5 (s), 36.6 (t), 52.0 (t), 68.5 (d), 112.2 (d), 120.3 (s), 124.0 (s), 145.9 (s), 161.3 (s), 194.1 (s). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.47; H, 7.63; N, 5.62. Found: C, 67.44; H, 7.55; N, 5.51].

Irradiation of 2c. A solution of **2c** (E/Z = 55/45; 0.4 g, 0.0081 M) in ether (220 mL) was irradiated for 20 min to give **3c** [62% yield; UV max (EtOH) 305.6 nm (ϵ 14 293)] as a mixture of isomers (trans/cis 55:45) which were separated by column chromatography [*cis*-**3c** ^{1}H NMR δ 1.10 (d, 3 H, J = 6.75 Hz), 1.38 (t, 3 H, J = 7 Hz), 1.80–2.60 (m, 6 H), 3.50 (dq, 1 H, J = 6.75 Hz, J = 10.5 Hz), 4.20 (q, 2 H, J = 7 Hz), 4.57 (d, 1 H, J = 10.5 Hz), 5.65 (br s, 1 H); ^{13}C NMR δ 14.3, 14.6, 22.3, 23.8, 36.3, 37.0, 61.3 (t), 64.4 (d), 113.6 (s), 168.1 (s), 171.0 (s), 192.2 (s); *trans*-**3c** ^{1}H NMR δ 1.25 (d, 3 H, J = 7 Hz), 1.32 (t, 3 H, J = 7 Hz), 1.80–3.00 (m, 7 H), 3.98 (d, 1 H, J = 6 Hz), 4.22 (q, 2 H, J = 7 Hz), 6.60 (br s, 1 H); ^{13}C NMR δ 14.1, 14.3, 20.7, 23.6, 36.2, 39.4, 61.1, 67.2, 112.5, 169.5, 172.6, 191.8] and **4c** [20% yield; mp 142–144 °C; UV max (EtOH) 284.7 nm (ϵ 14 217), 233.9 (23 071); ^{1}H NMR δ 1.42 (t, 3 H, J = 7 Hz), 2.0–3.0 (m, 6 H), 2.68 (s, 3 H), 4.40 (q, 2 H, J = 7 Hz), 9.0 (br s, 1 H); ^{13}C NMR δ 11.6, 14.4, 23.0, 23.4, 38.9, 60.6, 119.7, 120.1, 128.6, 146.3, 162.6, 195.9. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.16; H, 6.79; N, 6.33. Found: C, 64.94; H, 6.80; N, 6.27].

Irradiation of 2d. A solution of **2d** (E and Z isomers, E/Z = 65/35; 0.5 g; 0.0022 M) in ether (910 mL) was irradiated for 1 h to give **4d** [65% yield; mp 157–160 °C; ^{1}H NMR δ 1.1 (s, 6 H), 1.37 (t, 3 H, J = 7 Hz), 2.38 (s, 2 H), 2.65 (s, 2 H), 2.60 (s, 3 H), 4.32 (q, 2 H, J = 7 Hz); ^{13}C NMR δ 11.6 (q), 14.4 (q), 28.5 (q), 35.2 (s), 36.8 (t), 52.9 (t), 60.5 (t), 119.2 (s), 119.9 (s), 128.4 (s), 144.6 (s), 162.4 (s), 195.0 (s); exact mass 249.13704 (calcd for $C_{14}H_{19}NO_3$ 249.1365). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.47; H, 7.63; N, 5.62; O, 19.28. Found: C, 67.51; H, 7.61; N, 5.32; O, 19.46].

Irradiation of 2e. A solution of **2e** (1.2 g, 0.0076 M) in ether (550 mL) and THF (350 mL) was irradiated for 30 min to give **4e** [30% yield; ^{1}H NMR δ 1.80–2.90 (m, 6 H), 2.30 (s, 3 H), 4.0 (br s, 1 H); ^{13}C NMR (DMSO-d_6) δ 13.0, 24.4, 25.0, 101.7, 115.9, 120.2, 132.6, 149.4, 195.9].

Irradiation of 2f. A solution of **2f** (1 g, 0.0054 M) in ether (850 mL) and THF (50 mL) was irradiated for 35 min to give **4f** [33% yield; mp 108–112 °C; IR 3200, 2200, 1650, 1600 cm^{-1}; ^{1}H NMR δ 1.0 (s, 6 H), 2.25 (s, 2 H), 2.62 (s, 2 H), 2.27 (s, 3 H), 3.52 (br s, 1 H); ^{13}C NMR δ 12.8, 29.9, 36.9, 37.9, 54.2, 102.0, 115.8, 119.0, 148.1, 195.1; exact mass 202.1105 (calcd for $C_{12}H_{14}N_2O$ 202.1106). Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.29; H, 6.93; N, 13.86; O, 7.92. Found: C, 71.51; H, 6.93; N, 13.51; O, 7.82].

Irradiation of 2g. A solution of **2g** (2.5 g, 0.0131 M) in ether (710 mL) and benzene (200 mL) was irradiated for 90 min to give **3g** [46% yield; mp 136–139 °C; ^{1}H NMR δ 1.20 (d, 6 H, J = 6 Hz), 2.4–3.2 (m, 6 H), 4.80 (dd, 1 H, J = 8 Hz, J = 10.8 Hz), 5.0 (septet, 1 H, J = 6 Hz), 7.0 (br s, 1 H); ^{13}C NMR δ 21.7, 27.5 (t), 40.1 (t), 66.6 (d), 69.3 (d), 115.3 (s), 171.7 (s), 187.5 (s), 194.2 (s); exact mass 209.10523 (calcd for $C_{11}H_{15}NO_3$ 209.1051). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70; O, 22.97. Found: C, 62.87; H, 7.21; N, 6.53; O, 23.13] and **4g** [10% yield; mp 158–160 °C; ^{1}H NMR δ 1.30 (d, 6 H, J = 6 Hz), 2.9 (s, 4 H), 5.15 (septet,

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1 H, J = 6 Hz), 6.90 (s, 1 H), 10.7 (br s, 1 H); ^{13}C NMR δ 21.0 (t), 21.9 (q), 41.4 (t), 68.9 (d), 108.8 (d), 127.7 (s), 130.5 (s), 161.3 (s), 197.9 (s); exact mass 207.0893 (calcd for $C_{11}H_{13}NO_3$ 207.0894). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.77; H, 6.28; N, 6.76; O, 23.19. Found: C, 63.71; H, 6.37; N, 6.95; O, 23.45].

Irradiation of 2h. A solution of **2h** (E/Z = 50/50; 1.4 g, 0.0096 M) in ether was irradiated for 30 min to give **3h** as a mixture of isomers (trans/cis 50:50) which was separated by column chromatography [*trans*-**3h** 32% yield; ^{1}H NMR δ 1.28 (t, 3 H, J = 6.75 Hz), 1.35 (d, 3 H, J = 6.75 Hz), 2.20–2.90 (m, 4 H), 3.25 (dq, 1 H, J = 6 Hz, J = 6.75 Hz), 4.22 (q, 2H, J = 6.75 Hz), 4.35 (d, 1 H, J = 6 Hz), 7.30 (br s, 1 H); ^{13}C NMR δ 14.1 (q), 20.1 (q), 21.6 (t), 37.1 (d), 40.1 (t), 61.6 (t), 74.3 (d), 120.5 (s), 172.2 (s), 186.1 (s), 194.8 (s); *cis*-**3h** 18% yield; ^{1}H NMR δ 1.20 (t, 3 H, J = 7.5 Hz), 1.35 (d, 3 H, J = 7.5 Hz), 2.20–2.90 (m, 4 H), 3.40 (dq, 1 H, J = 7.5 Hz, J = 10.5 Hz), 4.25 (q, 2 H, J = 7.5 Hz), 5.0 (d, 1 H, J = 10.5 Hz), 7.10 (br s, 1 H); ^{13}C NMR δ 14.2, 14.4, 21.6, 34.6, 40.1, 61.3, 70.9, 120.7, 170.4, 186.3, 194.9] and **4h** [12% yield; mp 192–194 °C (lit.[18] mp 172–174 °C); ^{1}H NMR (DMSO-d_6) δ 1.33 (t, 3 H, J = 7.2 Hz), 2.34 (s, 3 H), 2.80 (s, 4 H), 4.30 (q, 2 H, J = 7.2 Hz), 12 (br s, 1 H); ^{13}C NMR (DMSO-d_6) δ 12.5 (q), 16.2 (q), 22.2 (t), 43.2, 61.8 (t), 124.2 (s), 127.0 (s), 128.4 (s), 161.9 (s), 163.1 (s), 198.8 (s); exact mass 207.08949 (calcd for $C_{11}H_{13}NO_3$ 207.0894). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.77; H, 6.28; N, 6.76. Found: C, 63.52; H, 6.29; N, 6.52].

Irradiation of 2i and 2j. A solution of **2i** or **2j** (0.4 g) in ether (250 mL) was irradiated for 20 min to yield polymers.

Irradiation of 2k. A solution of **2k** (1.3 g, 0.0197 M) in ether (290 mL) was irradiated for 3 h to give **4k** [31% yield; ^{1}H NMR δ 1.38 (d, 6 H, J = 6.5 Hz), 1.40 (t, 3 H, J = 6.6 Hz), 4.3 (q, 2 H, J = 6.6 Hz), 5.25 (septet, 1 H), 7.30 (m, 1 H), 7.58 (m, 1 H); ^{13}C NMR δ 14.4 (q), 22.0 (q), 60.2 (t), 68.5 (d), 116.0 (d), 117.9 (s), 124.2 (s), 127.5 (d), 161.0 (s), 164.4 (s). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.67; N, 6.22; O, 28.44. Found: C, 58.61; H, 6.89; N, 6.50; O, 28.21].

Irradiation of 2l. A solution of **2l** (1.2 g, 0.0196 M) in ether (290 mL) was irradiated for 1 h to give **4l** [22% yield; mp 134–136 °C; ^{1}H NMR δ 1.38 (d, 6 H, J = 6.5 Hz), 2.43 (s, 3 H), 2.60 (s, 3 H), 5.22 (septet, 1 H, J = 6.5 Hz), 7.23 (s, 1 H); ^{13}C NMR δ 14.0, 22.0, 28.3, 68.4, 117.3, 120.7, 122.3, 139.8, 161.1, 195.0. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70; O, 22.97. Found: C, 63.25; H, 7.12; N, 6.71; O, 23.02].

Irradiation of 2m. A solution of **2m** (0.8 g, 0.0168 M) in ether (210 mL) was irradiated for 20 min to give **4m** [20% yield; mp 70–72 °C (C_6H_6); ^{1}H NMR δ 1.30 (t, 6 H, J = 7 Hz), 2.60 (s, 3 H), 4.30 (q, 2 H, J = 7 Hz), 4.35 (q, 2 H, J = 7 Hz), 7.5 (d, 1 H, J = 3 Hz), 10.35 (br s, 1 H); ^{13}C NMR δ 11.4, 14.2, 14.5, 59.8, 60.5, 116.7, 121.0, 127.5, 129.9, 162.0, 165.0. Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.67; N, 6.22; O, 28.44. Found: C, 58.59; H, 6.78; N, 5.90; O, 28.24].

Irradiation of 2n. A solution of **2n** (0.7 g, 0.0157 M) in ether (210 mL) was irradiated for 30 min to give **4n** [57% yield; mp 140–142 °C (C_6H_6) (lit.[21] mp 142 °C); ^{1}H NMR δ 1.25 (t, 3 H, J = 7 Hz), 2.35 (s, 3 H), 2.45 (s, 3 H), 2.52 (s, 3 H), 4.28 (q, 2 H, J = 7 Hz), 10.3 (br s, 1 H); ^{13}C NMR δ 12.7, 14.5, 15.1, 31.3, 60.4, 118.1, 122.7, 123.6, 129.6, 138.7, 162.1, 195.8] and **5** [14% yield; ^{1}H NMR δ 1.40 (t, 3 H, J = 7.4 Hz), 2.30 (s, 3 H), 2.48 (s, 3 H), 2.50 (s, 3 H), 4.42 (q, 2 H, J = 7.4 Hz), 6.90 (s, 1 H); ^{13}C NMR δ 14.3, 19.5, 23.0, 24.3, 61.3, 122.3, 126.8, 145.3, 154.7, 154.7, 158.5, 169.1].

Irradiation of 6l. A solution of **6l** (Z configuration of the α,β-olefinic bond; 1 g) in ether (700 mL) was irradiated for 1 h to give **6l** (E configuration of the olefinic α,β-bond; 90% yield).

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Selective Reductions. 39. Partial Reduction of Carboxylic Acids with Thexylchloroborane–Methyl Sulfide. A Direct and Simple Aldehyde Synthesis

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A systematic study of the direct partial reduction of carboxylic acids to the corresponding aldehydes with thexylchloroborane–methyl sulfide (ThxBHCl·SMe_2) under practical conditions (methylene chloride, room temperature) has been carried out. The reaction is quite general, and the yields of aldehydes are very good, almost quantitative in the aliphatic series. Many other readily reducible functional groups tolerate these reaction conditions. Furthermore, aliphatic carboxylic acids can be reduced selectively in the presence of aromatic acids. The aldehyde products are readily isolated in high yields either by forming the sodium bisulfite adduct, followed by regeneration with formaldehyde, or by using steam distillation to remove the byproduct.

During the past 70 years, numerous efforts have been made to find simple and general synthetic routes to aldehydes from carboxylic acids.[2] In the early years, both the Rosenmund's catalytic hydrogenation of acid chlorides[3] and Stephen's procedure[4] were widely utilized. However, these procedures suffered from limited applicability. The discovery of lithium aluminum hydride[5] led to its application for the preparation of aldehydes by reduction of various carboxamides.[6,7]

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