136863-80-4; **2** (R = $CH_3CH_2C{\equiv}C(CH_2)_4$), 136863-81-5; **2** (R = $CH_3(CH_2)_2C{\equiv}C(CH_2)_4$), 136863-82-6; **2** (R = $CH_3OCH_2CH_2O(CH_2)_2$), 104779-00-2; **2** (R = $C_{18}H_{37}O(CH_2CH_2O)_3(CH_3)_2$), 136863-83-7; **2** (R = $(CH_2)_5N(CH_2O_2)$, 102475-03-6; **2** (R = $O(CH_2CH_2)_2N)CH_2)_2$), 102237-91-2; **2** (R = 3-butenyl), 127696-13-3; **2** (R = (*Z*)-2-hexenyl), 136863-84-8; **2** (R = (*E*)-2-tridecenyl), 136863-85-9; **2** (R = $CH_2CH_2CHMe_2$), 126156-74-9; **2** (R = ⟨15⟩CH_2), 104084-69-7; **2** (R = ⟨18⟩CH_2), 118921-90-7; **2** (R = 4-MeC_6H_4), 125507-32-6; **2** (R = Ph), 17613-65-9; AQ-1, 136863-86-0; AQ-2, 136863-87-1; $CH_3(CH_2)_2C{\equiv}C(CH_2)_4OH$, 68274-96-4; $C_{18}H_{37}O(CH_2CH_2O)_3H$, 4439-32-1; *n*-$C_3H_7OH$, 71-23-8; *n*-$C_4H_9OH$, 71-36-3; *n*-$C_8H_{17}OH$, 111-87-5; *n*-$C_9H_{19}OH$, 143-08-8; *n*-$C_{16}H_{33}OH$, 36653-82-4; $CH_2{=}CHCH_2OH$, 107-18-6; (*E*)-$CH_3CH{=}CHCH_2OH$, 504-61-0; (*Z*)-$CH_3CH{=}CHCH_2OH$, 4088-60-2; $C_6H_5CH_2OH$, 100-51-6; $CH_3C{\equiv}CH_2OH$, 764-01-2; $CH_3CH_2C{\equiv}CCH_2OH$, 6261-22-9; $CH_3(CH_2)_2C{\equiv}CCH_2OH$, 764-60-3; $CH_3C{\equiv}C(CH_2)_2OH$, 10229-10-4; $CH_3CH_2C{\equiv}C(CH_2)_2OH$, 1002-28-4; $CH_3(CH_2)_2C{\equiv}C(CH_2)_2OH$, 14916-79-1; $CH_3(CH_2)_4C{\equiv}C(CH_2)_2OH$, 31333-13-8; $CH_3C{\equiv}C(CH_2)_3OH$, 928-93-8; $CH_3CH_2C{\equiv}C(CH_2)_3OH$, 42397-24-0; $CH_3C{\equiv}C(CH_2)_4OH$, 58944-42-6; $CH_3CH_2C{\equiv}C(CH_2)_4OH$, 41547-21-1; $CH_3OCH_2CH_2OH$, 109-86-4; MeOEOEOH, 111-77-3; MeOEOEOEOH, 112-35-6; MeSEOH, 5271-38-5; $(CH_2)_5NCH_2CH_2OH$, 3040-44-6; $O(CH_2CH_2)_2NCH_2CH_2OH$, 622-40-2; $Me_2CHCH_2CH_2OH$, 123-51-3; $(CH_3)_2CHOH$, 67-63-0; $C_6H_{11}OH$, 108-93-0; MeOEOEOEOMe, 112-49-2; 18-crown-6, 17455-13-9; phenol, 108-95-2; 4-methylphenol, 106-44-5; (*E*)-2-hexanol, 928-95-0; 1,5-dichloroanthraquinone, 82-46-2; (*Z*)-2-hexenol, 928-94-9; (*E*)-2-tridecenol, 74962-98-4; 1,5-bis(hexadecyloxy)anthraquinone, 136892-84-7; 3-butenol, 627-27-0; 1-chloro-5-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]anthraquinone, 136863-88-2.

Supplementary Material Available: Solid-state experimental and supplementary references, ORTEP plots and details, and ^1H NMR spectra (65 pages). Ordering information is given on any current masthead page.

Regioselectivity of Rhodium(II)-Catalyzed Decomposition of 1-Alkyl-1-(diazoacetyl)alkenes. Synthesis of 2-Alkyl-2-cyclopentenones and 2-Alkylidenecyclopentanones

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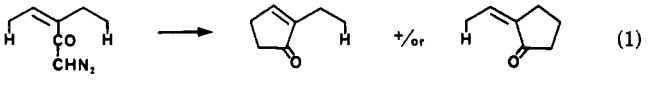
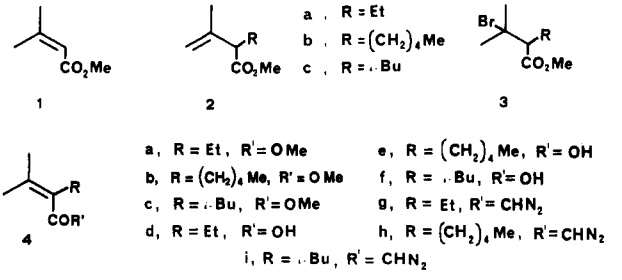
The synthesis of 1-alkyl-1-(diazoacetyl)alkenes and their dirhodium tetraacetate catalyzed transformation into 2-cyclopentenones and 2-alkylidenecyclopentanones are described. The competitive, intramolecular carbon–hydrogen insertion at two γ centers is discussed.

Recently there was introduced a new cyclopentenone synthesis based on rhodium(II)-catalyzed, intramolecular γ-carbon–hydrogen insertion of diazomethyl ketones derived from α,β-unsaturated acids.[1] Whereas the reaction revealed interesting features of stereochemistry (in some of the cases studied), it was unidirectional in view of the rigidity of the substrates and the proximity of the carbenoid carbon to only one γ-carbon center. It now became of interest to investigate the chemical behavior of diazomethyl ketones derived from α-alkyl α,β-unsaturated acids, thus exposing two γ-carbon sites to the carbenoid center and raising the question of regioselectivity of the reaction (eq 1). Nine cases, representing every combination of γ-methyl, γ-methylene, and γ-methine examples, were submitted to scrutiny.



(1)

Preparation of α,β-Unsaturated Acids. Alkylation of methyl senecioate (**1**)[2] with ethyl iodide, *n*-pentyl iodide, and isobutyl bromide under the influence of lithium diisopropylamide (LDA) furnished esters **2a**, **2b**, and **2c**, respectively. Treatment of the esters with hydrogen bromide in chloroform afforded bromo esters **3a**, **3b**, and **3c**, respectively, whose dehydrohalogenation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene[3] gave esters **4a**, **4b**, and **4c**, respectively. Finally, demethylation of these esters with trimethylsilyl iodide in carbon tetrachloride[4] yielded acids **4d**, **4e**, and **4f**, respectively.



The remaining α,β-unsaturated acids were prepared in a different manner, as follows. Triethyl α-phosphonobutyrate (**5a**),[5] triethyl α-phosphonohexanoate (**5b**), and methyl α-(diethoxyphosphinyl)isocaproate (**5c**) were obtained from their α-bromo ester equivalents and trialkyl

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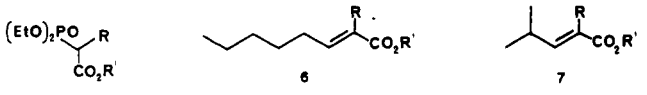
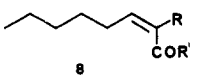
phosphites by a known procedure.[6] Exposure of the α-phosphono esters to ethanolic sodium ethoxide (or methanolic sodium methoxide) and hexanal led to *E*–*Z* pairs of olefinic esters **8a** and **6a**, **8b** and **6b**, and **8c** and **6c**, respectively. Similar reactions with isobutyraldehyde formed the following pairs of conjugated enoates: **9a**[7] and **7a**,[7] **9b** and **7b**, and **9c** and **7c**. Saponification of the esters produced acids **8d**, **8e**,[8] **8f**, **9d**, **9e**, and **9f**, respectively.



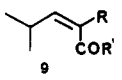
5 6 7

a, R=R'=Et; b, R=*n*-Bu, R'=Et; c, R=*i*-Bu, R'=Me



8

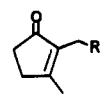
a, R = Et, R'=OEt
b, R=*n*-Bu, R'=OEt
c, R=*i*-Bu, R'=OMe
d, R = Et, R'=OH
e, R=*n*-Bu, R'=OH
f, R=*i*-Bu, R'=OH
g, R = Et, R'=CHN_2
h, R=*n*-Bu, R'=CHN_2
i, R=*i*-Bu, R'=CHN_2



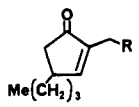
9

Diazo Ketone Decompositions. Treatment of acids **4d**, **4e**, **4f**, **8d**, **8e**, **8f**, **9d**, **9e**, and **9f** with oxalyl chloride in methylene chloride and the resultant acid chlorides with diazomethane and triethylamine in ether yielded diazo ketones **4g**, **4h**, **4i**, **8g**, **8h**, **8i**, **9g**, **9h**, and **9i**, respectively. The α-diazo carbonyl compounds were decomposed by slow addition of their dichloromethane solutions to stirring methylene chloride suspensions of dirhodium tetraacetate,[9] leading to cyclopentane derivatives in 54–80% yield.

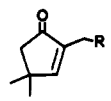
In this manner diazo compound **4g** was converted into cyclopentenone **10a**[10] (64% yield), **4h** into dihydrojasmone (**10b**)[11] and α-alkylidenecyclopentanone **13a** as a 1:1 mixture (80%), and **4i** into cyclopentenone **10c** and α-alkylidenecyclopentanone **13b**, also as a 1:1 mixture (65%).



10a, R= Me
b, R=*n*-Bu
c, R=*i*-Pr

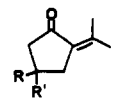


11a, R=Me
b, R=*n*-Pr
c, R=*i*-Pr

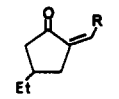


12a, R=Me
b, R=*n*-Pr
c, R=*i*-Pr

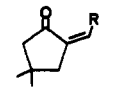
Similarly, diazo compound **8g** was transformed into cyclopentenone **11a** (70%), **8h** into cyclopentenone **11b** and α-alkylidenecyclopentanone **16a** as a 2:1 mixture (54%),[12,13] and **8i** into cyclopentenone **11c** and α-alkylidenecyclopentanone **15a** in the form of a 1:1 mixture (72%).



13a, R=*n*-Pr, R'=H
b, R=R'=Me



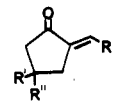
14a, R=$(CH_2)_4$Me
b, R=*i*-Pr



15a, R=$(CH_2)_4$Me
b, R=*i*-Pr

Finally, the decomposition of diazo ketones **9g**, **9h**, and **9i** led to cyclopentenone **12a** (62%), a 3:1 mixture (67%) of cyclopentenone **12b** and α-alkylidenecyclopentanone **14b**, and a 3:1 mixture (60%) of cyclopentenone **12c** and α-alkylidenecyclopentanone **15b**.

The alkylidenecyclopentanones **14** and **15** proved to be unstable and underwent isomerization (in nearly quantitative yield) into substances **16** in chloroform solution.



16a, R=$(CH_2)_4$Me, R'=Et, R''=H
b, R=$CHMe_2$, R'=Et, R''=H
c, R=$(CH_2)_4$Me, R'=R''=Me
d, R=$CHMe_2$, R'=R''=Me

Conclusion

Several facts emerge from the above reaction results. Cyclopentenone formation (**10a**, **11a** and **12a**) is the sole consequence of the carbon–hydrogen insertions of 1-(diazoacetyl)-1-ethylalkenes (**4g**, **8g**, and **9g**), i.e., the γ center adjacent to the olefinic bond shows much higher reactivity toward the carbenoid moiety than the methyl group of the saturated two-carbon side chain. Cyclopentenones (**10a**, **11b**, and **12c**) are the preferred products of diazo ketone decompositions (**4g**, **8h**, and **9f**) in cases in which the γ-carbon–hydrogen bond site on both sides of the diazoacetyl unit possesses the same substitution pattern (methyl vs methyl, methylene vs methylene, and methine vs methine moieties). Except for the 1-(diazoacetyl)-1-ethylalkene examples, the intramolecular carbon–hydrogen insertion processes show low regioselectivity.

Experimental Section

Melting points were obtained on a micro hot stage and are uncorrected. IR spectra were obtained with $CHCl_3$ solutions. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded at 200.1 and 50.3 MHz, respectively. Column chromatography was executed on 70–230-mesh Merck silica gel. All reactions were carried out under N_2, and all extracts were dried over Na_2SO_4.

Methyl 2-Alkyl-3-methyl-3-butenoates 2. A solution of 5.50 g (48 mmol) of methyl senecioate (1) in 20 mL of THF was added to a stirring solution of 55 mmol of LDA (prepared from *n*-butyllithium and diisopropylamine) in 60 mL of THF at −70 °C, and the stirring was continued for 1 h. The solution was allowed to warm to 0 °C, and 90 mmol of neat alkyl halide was added dropwise. The mixture was warmed to rt and stirred for 2 h. It was poured into water and extracted with $CHCl_3$. The extract was washed with water, dried, and evaporated. The residue was chromatographed and eluted with 25:1 hexane–ethyl acetate.

Methyl 2-ethyl-3-methyl-3-butenoate (2a): colorless liquid (75%); ^1H NMR δ 0.88 (t, 3, *J* = 7 Hz, ethyl Me), 1.6–2.0 (m, 2, ethyl CH_2), 1.73 (s, 3, 3-Me), 2.93 (t, 1, *J* = 7 Hz, H-2), 3.68 (s, 3, OMe), 4.8–5.0 (m, 2, C-4 Hs); ^{13}C NMR δ 11.6 (ethyl Me), 19.8 (3-Me), 23.1 (ethyl CH_2), 51.3 (OMe), 54.6 (C-2), 113.4 (C-4), 142.2 (C-3), 173.8 (C-1).

Anal. Calcd for $C_8H_{14}O_2$: C, 66.57; H, 9.92. Found: C, 66.66; H, 9.82.

Methyl 3-methyl-2-pentyl-3-butenoate (2b): colorless liquid (73%); ^1H NMR δ 0.83 (t, 3, *J* = 7 Hz, *n*-pent Me), 1.1–1.9 (m, 8, methylenes), 1.69 (s, 3, 3-Me), 2.98 (t, 1, *J* = 7 Hz, H-2), 3.64

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(12) The mixture could not be separated, but the two components could be characterized by spectral analysis. The component ratio is based on GC and NMR spectral analyses.
(13) In the transformation of the diazo ketones into α-alkylidenecyclopentanones, the stereochemical integrity of the double bond is maintained, as illustrated by the formation of ketones **14b** and **15** (vide infra). However, in the decomposition of diazo ketone **8c**, product **14a** could not be isolated in view of its spontaneous isomerization into ketone **16a**.

(s, 3, OMe), 4.8–4.9 (m, 2, C-4 Hs); ^{13}C NMR δ 13.7 (*n*-pent Me), 19.8 (3-Me), 22.3 (*n*-pent C-4), 27.0 (*n*-pent C-1), 30.0 (*n*-pent C-2), 31.5 (*n*-pent C-3), 51.2 (OMe), 52.9 (C-2), 113.2 (C-4), 142.4 (C-3), 173.7 (C-1).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.93. Found: C, 71.82; H, 10.63.

Methyl 2-isobutyl-3-methyl-3-butenoate (2c): colorless liquid (88%); ^1H NMR δ 0.84, 0.88 (d, 3 each, J = 7 Hz, methyls), 1.2–1.8 (m, 3, CH_2, CH), 1.71 (s, 3, 3-Me), 3.11 (t, 1, J = 7 Hz, H-2), 3.62 (s, 3, OMe), 4.8–4.9 (m, 2, C-4 Hs); ^{13}C NMR δ 19.9 (3-Me), 22.1 (Me), 22.4 (Me), 25.8 (*i*-Bu CH), 39.2 (*i*-Bu CH_2), 50.9 (OMe), 51.4 (C-2), 113.4 (C-4), 142.6 (C-3), 174.1 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.66; H, 10.52.

Methyl 2-Alkyl-3-methyl-2-butenoates 4a–c. A solution of 20 mmol of ester **2** in 150 mL of reagent grade $CHCl_3$ was saturated with HBr gas and then stirred for 6 h. It was concentrated to 50 mL, washed with water, dried, and evaporated. Bromo esters **3a** [^1H NMR δ 0.90 (t, 3, J = 7 Hz, ethyl Me), 1.5–1.9 (m, 2, CH_2), 1.74 (s, 6, methyls), 2.83 (t, 1, J = 7 Hz, H-2), 3.70 (s, 3, OMe)], **3b** [^1H NMR δ 0.85 (t, 3, J = 7 Hz, *n*-pent Me), 1.1–2.0 (m, 8, methylenes), 1.82 (s, 6, methyls), 2.83 (t, 1, J = 7 Hz, H-2), 3.72 (s, 3, OMe)], and **3c** [^1H NMR δ 0.88 (d, 6, J = 7 Hz, *i*-Bu methyls), 1.3–1.5 (m, 3, CH_2, CH), 1.74, 1.78 (s, 3 each, methyls), 2.90 (dd, 1, J = 12, 3 Hz, H-2), 3.64 (s, 3, OMe)] were used in the next reaction without further purification.

A solution of 15 mmol of bromo ester **3** and 4.50 g (30 mmol) of DBU in 80 mL of dry benzene was refluxed for 24 h. After concentration to 40 mL, it was poured into water and extracted with ether. The extract was washed with water, dried, and evaporated. The residue was chromatographed and eluted with 50:1 hexane–ethyl acetate.

Methyl 2-ethyl-3-methyl-2-butenoate (4a): colorless liquid (74%); ^1H NMR δ 0.92 (t, 3, J = 7 Hz, ethyl Me), 1.71 (s, 3, C-4 Hs), 1.86 [s, 3, 3(*Z*)-Me], 2.30 (q, 2, J = 7 Hz, CH_2), 3.72 (s, 3, OMe); ^{13}C NMR δ 13.6 (ethyl Me), 21.1 (C-4), 22.5 (3-Me), 22.9 (CH_2), 51.3 (OMe), 129.4 (C-2), 140.4 (C-3), 169.3 (C-1).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.62; H, 9.83.

Methyl 3-methyl-2-pentyl-2-butenoate (4b): colorless liquid (95%); ^1H NMR δ 0.88 (t, 3, J = 7 Hz, *n*-pent Me), 1.1–1.3 (m, 6, methylenes), 1.80 (s, 3, C-4 Hs), 1.94 [s, 3, 3(*Z*)-Me], 2.28 (t, 2, J = 8 Hz, allyl Hs), 3.70 (s, 3, OMe); ^{13}C NMR δ 13.7 (*n*-pent Me), 21.4 (C-4), 22.3 (3-Me), 22.6 (*n*-pent C-4), 28.7 (*n*-pent C-1), 29.7 (*n*-pent C-2), 31.5 (*n*-pent C-3), 50.7 (OMe), 128.1 (C-2), 141.1 (C-3), 170.0 (C-1).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.93. Found: C, 71.46; H, 11.08.

Methyl 2-isobutyl-3-methyl-2-butenoate (4c): colorless liquid (70%); ^1H NMR δ 0.86 (d, 6, J = 7 Hz, 2 Me), 1.65 (m, 1, CH), 1.78 (s, 3, C-4 Hs), 1.94 [s, 3, 3(*Z*)-Me], 2.22 (d, 2, J = 7 Hz, CH_2), 3.74 (s, 3, OMe); ^{13}C NMR δ 21.8 (C-4), 22.2 (Me), 22.2 (Me), 22.8 (3-Me), 28.4 (CH), 38.7 (CH_2), 50.9 (OMe), 128.3 (C-2), 141.2 (C-3), 170.6 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.49; H, 10.73.

2-Alkyl-3-methyl-2-butenoic Acids 4d–f. A solution of 10 mmol of methyl 2-alkyl-3-methyl-2-butenoate and 4.00 g (20 mmol) of trimethylsilyl iodide in 70 mL of CCl_4 was refluxed for 14 h. The mixture was poured into 100 mL of 15% sodium thiosulfate solution and extracted with $CHCl_3$. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 25:1 chloroform–ethyl acetate furnished the α,β-unsaturated acid.

2-Ethyl-3-methyl-2-butenoic acid (4d): colorless, viscous liquid (82%); ^1H NMR δ 1.03 (t, 3, J = 7 Hz, ethyl Me), 1.87 (s, 3, C-4 Hs), 2.09 [s, 3, 3(*Z*)-Me], 2.35 (q, 2, J = 7 Hz, CH_2); ^{13}C NMR δ 13.3 (Me), 22.4 (C-4), 22.9 (CH_2), 23.3 (3-Me), 128.3 (C-2), 146.8 (C-3), 175.2 (C-1).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.43. Found: C, 65.52; H, 9.51.

3-Methyl-2-pentyl-2-butenoic acid (4e): colorless, viscous liquid (91%); ^1H NMR δ 0.84 (t, 3, J = 7 Hz, *n*-pent Me), 1.1–1.6 (m, 6, methylenes), 1.83 (s, 3, C-4 Hs), 2.08 [s, 3, 3(*Z*)-Me], 2.31 (t, 2, J = 7 Hz, allyl Hs); ^{13}C NMR δ 14.0 (*n*-pent Me), 22.6 (*n*-pent C-4), 22.8 (C-4), 23.5 (3-Me), 29.8 (*n*-pent C-1 or C-2), 29.9 (*n*-pent C-2 or C-1), 31.9 (*n*-pent C-3), 127.4 (C-2), 146.5 (C-3), 174.8 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.76; H, 10.41.

2-Isobutyl-3-methyl-2-butenoic acid (4f): colorless, viscous liquid (75%); ^1H NMR δ 0.88 (d, 6, J = 7 Hz, methyls), 1.7–1.9 (m, 1, CH), 1.87 (s, 3, C-4 Hs), 2.08 [s, 3, 3(*Z*)-Me], 2.27 (d, 2, J = 7 Hz, CH_2); ^{13}C NMR δ 22.2 (Me), 22.2 (Me), 23.0 (C-4), 23.3 (3-Me), 28.5 (CH), 38.4 (CH_2), 126.8 (C-2), 146.3 (C-3), 175.8 (C-1).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.27; H, 10.21.

α-Phosphono Esters 5. The syntheses of triethyl α-phosphonohexanoate (**5b**) [colorless liquid (79%): bp 124–127 °C/3 Torr; ^1H NMR δ 0.91 (t, 3, J = 7 Hz, C-6 Hs), 1.1–1.5 (m, 4, C-4, C-5 Hs), 1.30 (t, 3, J = 7 Hz, ethoxy Me), 1.34 [td, 6, J = 7, 1 Hz, $P(OEt)_2$ methyls], 1.7–2.1 (m, 2, C-3 Hs), 2.93 (ddd, 1, J = 22, 12, 5 Hz, H-2), 4.0–4.3 (m, 4, 2 $POCH_2$), 4.24 (q, 2, J = 7 Hz, OCH_2)] from ethyl α-bromohexanoate and triethyl phosphite and of methyl α-(diethoxyphosphinyl)isocaproate (**5c**) [colorless liquid (82%): bp 112–115 °C/3 Torr; ^1H NMR δ 0.84, 0.86 (d, 3 each, J = 7 Hz, methyls), 1.28 (td, 6, J = 7, 1 Hz, ethoxy methyls), 1.4–1.7 (m, 2, C-3 Hs), 1.8–2.1 (m, 1, H-4), 3.00 (ddd, 1, J = 22, 12, 5 Hz, H-2), 3.67 (s, 3, OMe), 4.0–4.2 (m, 4, 2 OCH_2)] from methyl α-bromoisocaproate and triethyl phosphite followed a published procedure.[6] α-Phosphono esters **5** were used immediately in the next reaction.

Olefinic Esters 6–9. A solution of 10 mmol of phosphono ester **5** and 680 mg (10 mmol) of sodium ethoxide in 10 mL of dry ethanol (for the condensations of esters **5a** and **5b**), or 540 mg (10 mmol) of sodium methoxide in 10 mL of dry methanol (for the condensation of ester **5c**), was stirred for 15 min. A solution of 1.00 g (10 mmol) of hexanal, or 720 mg (10 mmol) of isobutyraldehyde, in 5 mL of dry ethanol (or methanol) was added dropwise and stirring continued for 6 h. The mixture was concentrated to 5 mL, diluted with water, and extracted with ether. The extract was washed with water, dried, and evaporated under vacuum. Medium-pressure liquid chromatography of the residue (crude olefinic esters as mixtures of *E* and *Z* isomers) on Merck silica gel 60 (0.068–0.200-mesh ASTM) with a Büchi 681 chromatography pump and elution with 50:1 hexane–ethyl acetate yielded the following α,β-unsaturated esters.

From Phosphonate 5a. Ethyl (*Z*)-2-ethyl-2-octenoate (8a): colorless liquid (28%); ^1H NMR δ 0.98 (t, 3, J = 6 Hz, C-8 Hs), 1.05 (t, 3, J = 7 Hz, Me), 1.2–1.5 (m, 6, methylenes), 1.32 (t, 3, J = 7 Hz, ethoxy Me), 2.26 (q, 2, J = 7 Hz, ethyl CH_2), 2.40 (m, 2, C-4 Hs), 4.20 (q, 2, J = 7 Hz, OCH_2), 5.84 (tm, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.6 (Me), 14.0 (Me), 14.2 (Me), 22.5 (C-7), 27.6 (ethyl CH_2), 29.2 (C-5 or C-4), 29.5 (C-4 or C-5), 31.6 (C-6), 59.8 (OCH_2), 133.8 (C-2), 140.2 (C-3), 168.2 (C-1).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.52; H, 11.26.

Ethyl (*E*)-2-ethyl-2-octenoate (6a): colorless liquid (37%); ^1H NMR δ 0.88 (t, 3, J = 6 Hz, C-8 Hs), 0.95 (t, 3, J = 7 Hz, Me), 1.1–1.5 (m, 6, methylenes), 1.23 (t, 3, J = 7 Hz, ethoxy Me), 2.16 (q, 2, J = 7 Hz, ethyl CH_2), 2.26 (m, 2, C-4 Hs), 4.16 (q, 2, J = 7 Hz, OCH_2), 6.70 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.8 (Me), 13.8 (Me), 14.2 (Me), 20.0 (ethyl CH_2), 22.4 (C-7), 28.2 (C-4 or C-5), 28.5 (C-5 or C-4), 31.6 (C-6), 60.1 (OCH_2), 134.0 (C-2), 141.9 (C-3), 167.9 (C-1).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.78; H, 11.09.

Ethyl (*Z*)-2-ethyl-4-methyl-2-pentenoate (9a): colorless liquid (38%); ^1H NMR spectrally identical with reported data;[7] ^{13}C NMR δ 13.5 (Me), 14.2 (Me), 22.7 (C-5), 22.7 (4-Me), 27.4 (ethyl CH_2), 28.2 (C-4), 59.8 (OCH_2), 131.6 (C-2), 146.3 (C-3), 168.3 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.46; H, 10.79.

Ethyl (*E*)-2-ethyl-4-methyl-2-pentenoate (7a): colorless liquid (35%); ^1H NMR spectrally identical with reported data;[7] ^{13}C NMR δ 14.0 (Me), 14.1 (Me), 19.9 (ethyl CH_2), 22.1 (C-5), 22.1 (4-Me), 27.6 (C-4), 59.9 (OCH_2), 131.7 (C-2), 147.9 (C-3), 167.7 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.64; H, 10.56.

From Phosphonate 5b. Ethyl (*Z*)-2-butyl-2-octenoate (8b): colorless liquid (25%); ^1H NMR δ 0.90, 0.90 (t, 3 each, J = 6 Hz, *n*-Bu Me, C-8 Hs), 1.2–1.5 (m, 10, methylenes), 1.29 (t, 3, J = 7

Hz, ethoxy Me), 2.25 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 2.40 (dt, 2, J = 8, 8 Hz, C-4 Hs), 4.20 (q, 2, J = 7 Hz, OCH_2), 5.83 (t, 1, J = 9 Hz, H-3); ^{13}C NMR δ 13.8 (ethoxy Me), 14.2 (n-Bu Me), 14.2 (C-8), 22.1 (C-7 or n-Bu C-3), 22.4 (n-Bu C-3 or C-7), 29.1 (C-5 or C-4), 29.4 (C-4 or C-5), 31.3 (C-6 or n-Bu C-1), 31.5 (n-Bu C-1 or C-6), 59.8 (OCH_2), 132.3 (C-2), 140.8 (C-3), 168.2 (C-1).

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.57. Found: C, 74.35; H, 11.45.

Ethyl (*E*)-2-butyl-2-octenoate (6b): colorless liquid (60%); ^1H NMR δ 0.92, 0.93 (t, 3 each, J = 6 Hz, n-Bu Me, C-8 Hs), 1.2–1.6 (m, 10, methylenes), 1.30 (t, 3, J = 7 Hz, ethoxy Me), 2.18 (dt, 2, J = 8, 8 Hz, C-4 Hs), 2.30 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 4.20 (q, 2, J = 7 Hz, OCH_2), 6.74 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.8 (ethoxy Me), 14.1 (n-Bu Me), 14.1 (C-8), 22.4 (C-7 or n-Bu C-3), 22.6 (n-Bu C-3 or C-7), 28.4 (C-4), 28.4 (C-5), 31.5 (C-6), 31.5 (n-Bu C-2), 60.1 (OCH_2), 132.5 (C-2), 142.2 (C-3), 167.9 (C-1).

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.57. Found: C, 74.21; H, 11.66.

Ethyl (*Z*)-2-butyl-4-methyl-2-pentenoate (9b): colorless liquid (40%); ^1H NMR δ 0.82 (t, 3, J = 7 Hz, n-Bu Me), 0.92, 0.92 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.2–1.4 (m, 4, methylenes), 1.23 (t, 3, J = 7 Hz, ethoxy Me), 2.1–2.2 (m, 2, n-Bu C-1 Hs), 3.02 (m, 1, H-4), 4.12 (q, 2, J = 7 Hz, OCH_2), 5.52 (dt, 1, J = 10, 1 Hz, H-3); ^{13}C NMR δ 13.6 (ethoxy Me), 14.0 (n-Bu Me), 22.0 (n-Bu C-3), 22.6 (C-5), 22.6 (4-Me), 28.2 (C-4), 31.1 (n-Bu C-1), 34.1 (n-Bu C-2), 59.7 (OCH_2), 130.1 (C-2), 147.1 (C-3), 168.1 (C-1).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.76; H, 11.13.

Ethyl (*E*)-2-butyl-4-methyl-2-pentenoate (7b): colorless liquid (25%); ^1H NMR δ 0.85 (t, 3, J = 6 Hz, n-Bu Me), 0.96, 0.96 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.2–1.4 (m, 4, methylenes), 1.24 (t, 3, J = 7 Hz, ethoxy Me), 2.23 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 2.5–2.7 (m, 1, H-4), 4.12 (q, 2, J = 7 Hz, OCH_2), 6.47 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 13.7 (ethoxy Me), 14.1 (n-Bu Me), 22.2 (C-5), 22.2 (4-Me), 22.5 (n-Bu C-3), 26.4 (n-Bu C-1), 27.6 (C-4), 31.9 (n-Bu C-2), 60.0 (OCH_2), 130.4 (C-2), 148.4 (C-3), 168.1 (C-1).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 72.68; H, 11.18. Found: C, 72.67; H, 11.09.

From Phosphonate 5c. Methyl (*Z*)-2-isobutyl-2-octenoate (8c): colorless liquid (12%); ^1H NMR δ 0.87, 0.87 (d, 3 each, J = 7 Hz, i-Bu methyls), 0.89 (t, 3, J = 7 Hz, C-8 Hs), 1.2–1.5 (m, 6, methylenes), 1.6–1.8 (m, 1, i-Bu CH), 2.32 (d, 2, J = 7 Hz, i-Bu CH_2), 2.40 (dt, 2, J = 8, 8 Hz, C-4 Hs), 3.73 (s, 3, OMe), 5.82 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.9 (C-8), 22.1 (i-Bu Me), 22.1 (i-Bu Me), 22.4 (C-7), 27.5 (i-Bu CH), 29.1 (C-5), 29.5 (C-4), 31.4 (C-6), 43.9 (i-Bu CH_2), 50.9 (OMe), 130.9 (C-2), 142.7 (C-3), 168.7 (C-1).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.62; H, 11.26.

Methyl (*E*)-2-isobutyl-2-octenoate (6c): colorless liquid (34%); ^1H NMR δ 0.88, 0.88 (d, 3 each, J = 7 Hz, i-Bu methyls), 0.89 (t, 3, J = 7 Hz, C-8 Hs), 1.2–1.5 (m, 6, methylenes), 1.6–1.9 (m, 1, i-Bu CH), 2.20 (d, 2, J = 7 Hz, i-Bu CH_2), 2.40 (dt, 2, J = 8, 8 Hz, C-4 Hs), 3.68 (s, 3, OMe), 6.73 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.8 (C-8), 22.3 (C-7), 22.4 (i-Bu Me), 22.4 (i-Bu Me), 28.2 (i-Bu CH), 28.4 (C-5), 28.7 (C-4), 31.5 (C-6), 35.5 (i-Bu CH_2), 51.3 (OMe), 131.3 (C-2), 143.2 (C-3), 168.5 (C-1).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.58; H, 11.39. Found: C, 73.42; H, 11.45.

Methyl (*Z*)-2-isobutyl-4-methyl-2-pentenoate (9c): colorless liquid (30%); ^1H NMR δ 0.85, 0.85 (d, 3 each, J = 7 Hz, i-Bu methyls), 0.99, 0.99 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.6–1.8 (m, 1, i-Bu CH), 2.09 (d, 2, J = 8 Hz, i-Bu CH_2), 3.0–3.2 (m, 1, H-4), 3.69 (s, 3, OMe), 5.58 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 21.8 (Me), 21.8 (Me), 22.5 (Me), 22.5 (Me), 27.2 (i-Bu CH), 28.2 (C-4), 43.8 (i-Bu CH_2), 50.6 (OMe), 128.7 (C-2), 148.8 (C-3), 168.3 (C-1).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.93. Found: C, 71.76; H, 10.82.

Methyl (*E*)-2-isobutyl-4-methyl-2-pentenoate (7c): colorless liquid (25%); ^1H NMR δ 0.88, 0.88 (d, 3 each, J = 7 Hz, i-Bu methyls), 1.01, 1.01 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.6–1.9 (m, 1, i-Bu CH), 2.19 (d, 2, J = 8 Hz, i-Bu CH_2), 2.5–2.8 (m, 1, H-4), 3.70 (s, 3, OMe), 6.57 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 21.9 (Me), 21.9 (Me), 22.2 (Me), 22.2 (Me), 27.9 (i-Bu CH), 28.0 (C-4), 35.4 (i-Bu CH_2), 51.2 (OMe), 128.9 (C-2), 149.4 (C-3), 168.8 (C-1).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.93. Found: C, 71.59; H, 11.02.

Saponification of Esters 8 and 9. A solution of 10 mmol of the α,β-unsaturated ester in 150 mL of 10% methanolic KOH was kept at 40 °C for 8 h and then concentrated to 60 mL by vacuum distillation. It was poured into 140 mL of water and extracted with $CHCl_3$. The aqueous solution was acidified with 2% H_2SO_4 and extracted with $CHCl_3$. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 25:1 $CHCl_3$–EtOAc furnished α,β-unsaturated acid.

(*Z*)-2-Ethyl-2-octenoic acid (8d): colorless, viscous liquid (82%); ^1H NMR δ 0.93 (t, 3, J = 6 Hz, C-8 Hs), 1.04 (t, 3, J = 7 Hz, ethyl Me), 1.1–1.3 (m, 6, methylenes), 2.16 (q, 2, J = 7 Hz, ethyl CH_2), 2.28 (dt, 2, J = 8, 8 Hz, C-4 Hs), 6.03 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.8 (ethyl Me), 13.9 (C-8), 22.5 (C-7), 27.4 (ethyl CH_2), 29.2 (C-5), 29.7 (C-4), 31.5 (C-6), 132.7 (C-2), 144.7 (C-3), 174.1 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.43; H, 10.79.

(*Z*)-2-Butyl-2-octenoic acid (8e):[8] colorless liquid (80%); ^1H NMR δ 0.98, 0.98 (t, 3 each, J = 6 Hz, n-Bu Me, C-8 Hs), 1.1–1.7 (m, 10, methylenes), 2.20 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 2.40 (dt, 2, J = 8, 8 Hz, C-4 Hs), 5.86 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.9 (C-8), 14.0 (n-Bu Me), 22.3 (n-Bu C-3), 22.5 (C-7), 29.2 (C-5), 29.8 (C-4), 31.6 (C-6), 31.6 (n-Bu C-1), 34.2 (n-Bu C-2), 131.3 (C-2), 145.6 (C-3), 174.2 (C-1).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.80; H, 11.09.

(*Z*)-2-Isobutyl-2-octenoic acid (8f): colorless liquid (86%); ^1H NMR δ 0.87, 0.87 (d, 3 each, J = 7 Hz, i-Bu methyls), 0.89 (t, 3, J = 6 Hz, C-8 Hs), 1.2–1.6 (m, 6, methylenes), 1.7–1.9 (m, 1, i-Bu CH), 2.12 (d, 2, J = 8 Hz, i-Bu CH_2), 2.51 (dt, 2, J = 8, 8 Hz, C-4 Hs), 5.98 (t, 1, J = 8 Hz, H-3); ^{13}C NMR δ 13.9 (C-8), 22.1 (i-Bu Me), 22.1 (i-Bu Me), 22.5 (C-7), 27.5 (i-Bu CH), 29.2 (C-5), 29.7 (C-4), 31.5 (C-6), 43.9 (i-Bu CH_2), 130.2 (C-2), 146.6 (C-3), 174.2 (C-1).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.59; H, 11.39.

(*Z*)-2-Ethyl-4-methyl-2-pentenoic acid (9d): colorless, viscous liquid (84%); ^1H NMR δ 0.99, 0.99 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.08 (t, 3, J = 7 Hz, ethyl Me), 2.26 (q, 2, J = 7 Hz, ethyl CH_2), 3.2–3.4 (m, 1, H-4), 5.80 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 13.8 (ethyl Me), 22.7 (4-Me), 22.7 (C-5), 27.3 (ethyl CH_2), 28.3 (C-4), 130.4 (C-2), 150.9 (C-3), 174.2 (C-1).

Anal. Calcd for $C_8H_{14}O_2$: C, 68.57; H, 9.92. Found: C, 68.46; H, 9.99.

(*Z*)-2-Butyl-4-methyl-2-pentenoic acid (9e): colorless liquid (80%); ^1H NMR δ 0.90 (t, 3, J = 6 Hz, n-Bu Me), 0.98, 0.98 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.1–1.6 (m, 4, methylenes), 2.24 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 3.1–3.6 (m, 1, H-4), 5.80 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 13.6 (n-Bu Me), 22.0 (n-Bu C-3), 22.5 (4-Me), 22.5 (C-5), 28.2 (C-4), 31.3 (n-Bu C-1), 33.9 (n-Bu C-2), 128.9 (C-2), 151.5 (C-3), 174.1 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.48; H, 10.73.

(*Z*)-2-Isobutyl-4-methyl-2-pentenoic acid (9f): colorless liquid (74%); ^1H NMR δ 0.85, 0.85 (d, 3 each, J = 7 Hz, i-Bu methyls), 1.02, 1.02 (d, 3 each, J = 7 Hz, 4-Me, C-5 Hs), 1.7–1.9 (m, 1, i-Bu CH), 2.09 (d, 2, J = 7 Hz, i-Bu CH_2), 3.2–3.4 (m, 1, H-4), 5.65 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 22.1 (Me), 22.1 (Me), 22.7 (Me), 22.7 (Me), 27.5 (i-Bu CH), 28.6 (C-4), 43.8 (i-Bu CH_2), 127.9 (C-2), 152.8 (C-3), 174.3 (C-1).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.63; H, 10.56.

Preparation of Diazo Ketones. Freshly distilled oxalyl chloride (2.50 g, 20 mmol) was added dropwise to a stirring solution of 10 mmol of α,β-unsaturated acid in 15 mL of dry CH_2Cl_2 at 35 °C, and the stirring was continued for 2 h. The solution was evaporated under vacuum, and the residual α,β-unsaturated acid chloride was dissolved in 100 mL of dry ether. The solution was added dropwise over a 0.5-h period to a stirring solution of 13 mmol of diazomethane and 10 mmol of distilled triethylamine in 50 mL of anhydrous ether at 0 °C, and the stirring was continued for 2 h. The mixture was filtered, and the filtrate was evaporated. Chromatography of the residue through a short

column of neutral alumina (activity III) and elution with 25:1 hexane–ethyl acetate led to the diazo ketone, which was used in the next reaction without further purification.

1-Diazo-3-ethyl-4-methyl-3-penten-2-one (4g): yellow, amorphous solid (42%); IR C=N_2 2100 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 1.00 (t, 3, J = 7 Hz, ethyl Me), 1.78, 1.86 (s, 3 each, methyls), 2.28 (q, 2, J = 7 Hz, CH_2), 5.26 (s, 1, H-1).

1-Diazo-3-pentyl-4-methyl-3-penten-2-one (4h): yellow, viscous liquid (45%); IR CHN_2 2862 (m), C=N_2 2100 (s), C=O 1610 (s) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, n-pent Me), 1.1–1.6 (m, 6, methylenes), 1.74, 1.84 (s, 3 each, methyls), 2.18 (t, 2, J = 7 Hz, n-pent C-1 Hs), 5.24 (s, 1, H-1).

1-Diazo-3-isobutyl-4-methyl-3-penten-2-one (4i): pale yellow, amorphous solid (44%); IR CHN_2 2862 (m), C=N_2 2098 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 0.88, 0.88 (d, 3 each, J = 7 Hz, i-Bu methyls), 1.5–1.8 (m, 1, i-Bu CH), 1.72, 1.84 (s, 3 each, methyls), 2.13 (d, 2, J = 8 Hz, i-Bu CH_2), 5.25 (s, 1, H-1).

(Z)-1-Diazo-3-ethyl-3-nonen-2-one (8g): pale yellow, amorphous solid (34%); IR CHN_2 2860 (m), C=N_2 2095 (s), C=O 1590 (s) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, C-10 Hs), 1.04 (t, 3, J = 7 Hz, ethyl Me), 1.2–1.5 (m, 6, methylenes), 2.1–2.4 (m, 4, ethyl CH_2, C-5 Hs), 5.31 (s, 1, H-1), 5.54 (t, 1, J = 8 Hz, H-4).

(Z)-3-Butyl-1-diazo-3-nonen-2-one (8h): yellow, viscous liquid (42%); IR CHN_2 2860 (m), C=N_2 2100 (s), C=O 1605 (s) cm^{-1}; ^1H NMR δ 0.90, 0.90 (t, 3 each, J = 7 Hz, n-Bu Me, C-9 Hs), 1.0–1.7 (m, 10, methylenes), 2.0–2.5 (m, 4, n-Bu C-1 Hs, C-5 Hs), 5.28 (s, 1, H-1), 5.52 (t, 1, J = 8 Hz, H-4).

(Z)-3-Isobutyl-1-diazo-3-nonen-2-one (8i): yellow, viscous liquid (42%); IR C=N_2 2100 (s), C=O 1610 (s) cm^{-1}; ^1H NMR δ 0.83, 0.83 (d, 3 each, J = 7 Hz, methyls), 0.84 (t, 3, J = 6 Hz, C-9 Hs), 1.1–1.9 (m, 7, CH, methylenes), 2.10 (d, 2, J = 8 Hz, i-Bu CH_2), 2.1–2.4 (m, 2, C-5 Hs), 5.26 (s, 1, H-1), 5.50 (t, 1, J = 8 Hz, H-4).

(Z)-1-Diazo-3-ethyl-5-methyl-3-hexen-2-one (9g): yellow, viscous liquid (40%); IR CHN_2 2862 (m), C=N_2 2100 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 0.98, 0.98 (d, 3 each, J = 7 Hz, methyls), 1.04 (t, 3, J = 7 Hz, ethyl Me), 2.21 (q, 2, ethyl CH_2), 2.7–3.0 (m, 1, H-5), 5.30 (d, 1, J = 10 Hz, H-4), 5.35 (s, 1, H-1).

(Z)-3-Butyl-1-diazo-5-methyl-3-hexen-2-one (9h): pale yellow, amorphous solid (44%); IR CHN_2 2865 (m), C=N_2 2100 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 0.90 (t, 3, J = 6 Hz, n-Bu Me), 0.94, 0.94 (d, 3 each, J = 7 Hz, methyls), 1.1–1.5 (m, 4, methylenes), 2.12 (t, 2, J = 8 Hz, n-Bu C-1 Hs), 2.5–3.0 (m, 1, H-5), 5.21 (s, 1, H-1), 5.23 (d, 1, J = 10 Hz, H-4).

(Z)-3-Isobutyl-1-diazo-5-methyl-3-hexen-2-one (9i): yellow, viscous liquid (38%); IR C=N_2 2098 (s), C=O 1610 (s) cm^{-1}; ^1H NMR δ 0.88, 0.88 (d, 3 each, J = 7 Hz, i-Bu methyls), 1.01, 1.01 (d, 3, J = 7 Hz, methyls), 1.5–1.9 (m, 1, i-Bu CH), 2.05 (d, 2, J = 8 Hz, i-Bu CH_2), 2.6–3.1 (m, 1, H-5), 5.30 (s, 1, H-1), 5.34 (d, 1, J = 10 Hz, H-4).

Diazo Ketone Decompositions. A solution of 2 mmol of diazo ketone in 150 mL of CH_2Cl_2 was added dropwise over a 6-h period to a suspension of 0.04 mmol of dirhodium tetraacetate in 50 mL of CH_2Cl_2. The mixture was evaporated under vacuum. Chromatography of the residue and elution with 30:1 hexane–ethyl acetate yielded the cyclopentenone and α-alkylidenecyclopentanone.

2-Ethyl-3-methyl-2-cyclopentenone (10a):[10] colorless liquid (64%); IR C=O 1690 (s), C=C 1620 (w) cm^{-1}; ^1H NMR δ 0.98 (t, 3, J = 7 Hz, ethyl Me), 2.07 (s, 3, Me), 2.18 (q, 2, J = 7 Hz, ethyl CH_2), 2.3–2.4 (m, 2, C-5 Hs), 2.4–2.6 (m, 2, C-4 Hs); ^{13}C NMR δ 12.8 (ethyl Me), 16.2 (Me), 29.6 (ethyl CH_2), 31.5 (C-4), 34.3 (C-5), 140.0 (C-2), 169.2 (C-3), 209.3 (C-1).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.42; H, 9.67.

Dihydrojasmone (10b): colorless liquid (40%); IR, ^1H NMR and ^{13}C NMR spectrally identical with recorded data.[11]

2-Isopropylidene-4-propylcyclopentanone (13a): colorless liquid (40%); IR C=O 1700 (s), C=C 1630 (s) cm^{-1}; ^1H NMR δ 0.90 (t, 3, J = 6 Hz, n-Pr Me), 1.2–1.5 (m, 4, n-Pr methylenes), 1.82, 2.20 (s, 3 each, methyls), 1.98 (dd, 1, J = 17, 7 Hz, H-5), 2.0–2.2 (m, 2, H-3, H-4), 2.45 (dd, 1, J = 17, 6 Hz, H-5), 2.75 (dd, 1, J = 16, 7 Hz, H-3); ^{13}C NMR δ 14.1 (n-Pr Me), 20.4 (Me), 20.7 (n-Pr C-2), 24.3 (Me), 32.8 (C-4), 36.1 (C-3), 38.3 (n-Pr C-1), 47.2 (C-5), 131.3 (C-2), 146.6 (olefinic C), 206.9 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.60; H, 10.83.

2-Isobutyl-3-methyl-2-cyclopentenone (10c): colorless liquid (33%); IR C=O 1680 (s), C=C 1630 (s) cm^{-1}; ^1H NMR δ 0.80, 0.80 (d, 3 each, J = 7 Hz, i-Bu methyls), 1.6–1.9 (m, 1, i-Bu CH), 2.00 (s, 3, Me), 2.03 (d, 2, J = 7 Hz, i-Bu CH_2), 2.2–2.4 (m, 2, C-5 Hs), 2.4–2.5 (m, 2, C-4 Hs); ^{13}C NMR δ 17.3 (3-Me), 22.4 (Me), 22.4 (Me), 27.6 (i-Bu CH), 31.4 (C-4), 32.0 (i-Bu CH_2), 34.3 (C-5), 140.0 (C-2), 170.3 (C-3), 209.5 (C-1).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.96; H, 10.48.

2-Isopropylidene-4,4-dimethylcyclopentanone (13b): colorless liquid (32%); IR C=O 1695 (s), C=C 1620 (s) cm^{-1}; ^1H NMR δ 1.15, 1.15 (s, 3 each, C-4 methyls), 1.77, 2.18 (s, 3 each, methyls), 2.14 (s, 2, C-5 Hs), 2.37 (br s, 2, C-3 Hs); ^{13}C NMR δ 20.4 (Me), 24.1 (Me), 28.7 (4-Me), 28.7 (4-Me), 32.7 (C-4), 44.4 (C-3), 55.2 (C-5), 131.6 (C-2), 147.1 (olefinic C), 206.7 (C-1).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.67.

4-Butyl-2-ethyl-2-cyclopentenone (11a): colorless liquid (70%); IR C=O 1685 (s), C=C 1622 (w) cm^{-1}; ^1H NMR δ 0.86 (t, 3, J = 6 Hz, n-Bu Me), 1.05 (t, 3, J = 7 Hz, ethyl Me), 1.3–1.7 (m, 6, methylenes), 2.00 (dd, 1, J = 19, 2 Hz, H-5), 2.13 (q, 2, J = 7 Hz, ethyl CH_2), 2.53 (dd, 1, J = 19, 7 Hz, H-5), 2.7–2.9 (m, 1, H-4), 7.1–7.3 (m, 1, H-3); ^{13}C NMR δ 11.9 (ethyl Me), 13.8 (n-Bu Me), 17.8 (ethyl CH_2), 22.6 (n-Bu C-3), 29.7 (n-Bu C-2), 34.8 (n-Bu C-1), 38.6 (C-4), 41.7 (C-5), 147.0 (C-2), 160.2 (C-3), 209.1 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.38; H, 11.00.

2,4-Dibutyl-2-cyclopentenone (11b) and (E)-4-ethyl-2-hexylidenecyclopentanone (16a): colorless, liquid mixture (54%).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.42; H, 11.49.

Ketone 11b (36%): ^1H NMR δ 0.88, 0.88 (t, 3 each, J = 6 Hz, methyls), 1.1–1.5 (m, 10, methylenes), 2.00 (dd, 1, J = 19, 2 Hz, H-5), 2.15 (t, 2, J = 8 Hz, 2-n-Bu C-1 Hs), 2.55 (dd, 1, J = 19, 7 Hz, H-5), 2.6–2.8 (m, 1, H-4), 7.1–7.2 (m, 1, H-3); ^{13}C NMR δ 13.7 (Me), 13.8 (Me), 22.4 (2-n-Bu C-3), 22.7 (4-n-Bu C-3), 24.3 (2-n-Bu C-1), 29.7 (2-n-Bu C-2), 29.9 (4-n-Bu C-2), 34.9 (4-n-Bu C-1), 38.7 (C-4), 41.6 (C-5), 145.7 (C-2), 161.0 (C-3), 209.3 (C-1).

Ketone 16a (18%): ^1H NMR δ 0.88, 0.88 (t, 3 each, J = 6 Hz, methyls), 1.1–1.6 (m, 9, CH, methylenes), 2.0–2.2 (m, 2, C-5 Hs), 2.6–2.8 (m, 2, C-3 Hs), 6.4–6.5 (m, 1, olefinic H); ^{13}C NMR δ 11.8 (ethyl Me), 13.6 (Me), 22.4 (n-Hex C-5), 28.0 (n-Hex C-3), 28.7 (ethyl CH_2), 29.4 (n-Hex C-2), 31.4 (n-Hex C-4), 35.4 (C-4), 38.7 (C-3), 45.0 (C-5), 135.9 (C-2), 137.6 (olefinic CH), 206.4 (C-1).

4-Butyl-2-isobutyl-2-cyclopentenone (11c): colorless liquid (36%); IR C=O 1685 (s), C=C 1620 (w) cm^{-1}; ^1H NMR δ 0.88, 0.88 (d, 3 each, J = 6 Hz, i-Bu methyls), 0.90 (t, 3, J = 6 Hz, Me), 1.2–1.7 (m, 6, methylenes), 1.7–2.0 (m, 1, i-Bu CH), 2.03 (dd, 1, J = 19, 2 Hz, H-5), 2.05 (d, 2, J = 7 Hz, i-Bu CH_2), 2.58 (dd, 1, J = 19, 7 Hz, H-5), 2.7–2.9 (m, 1, H-4), 7.2–7.3 (m, 1, H-3); ^{13}C NMR δ 13.9 (n-Bu Me), 22.4 (Me), 22.4 (Me), 22.7 (n-Bu C-3), 27.0 (i-Bu CH), 29.8 (n-Bu C-2), 33.8 (i-Bu CH_2), 35.0 (n-Bu C-1), 38.8 (C-4), 41.6 (C-5), 144.5 (C-2), 162.3 (C-3), 209.4 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 80.35; H, 11.41. Found: C, 80.46; H, 11.36.

(Z)-2-Hexylidene-4,4-dimethylcyclopentanone (15a): colorless liquid (36%); IR C=O 1708 (s), C=C 1640 (s) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 6 Hz, n-Hex Me), 1.10, 1.10 (s, 3 each, methyls), 1.1–1.6 (m, 6, methylenes), 2.0–2.2 (m, 2, n-Hex C-2 Hs), 2.18 (s, 2, C-5 Hs), 2.38 (s, 2, C-3 Hs), 6.4–6.7 (m, 1, olefinic H); ^{13}C NMR δ 13.9 (n-Hex Me), 22.4 (n-Hex C-5), 28.3 (Me), 28.3 (Me), 28.6 (n-Hex C-3), 29.0 (n-Hex C-2), 31.5 (n-Hex C-4), 33.8 (C-4), 46.5 (C-3), 55.5 (C-5), 135.9 (C-2), 141.4 (n-Hex C-1), 204.8 (C-1).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.44; H, 11.32.

2-Ethyl-4,4-dimethyl-2-cyclopentenone (12a): colorless liquid (62%); IR C=O 1685 (s), C=C 1627 (w) cm^{-1}; ^1H NMR δ 1.08 (t, 3, J = 7 Hz, ethyl Me), 1.20, 1.20 (s, 3 each, methyls), 2.14 (q, 2, J = 7 Hz, ethyl CH_2), 2.26 (s, 2, C-5 Hs), 7.04 (s, 1, H-3); ^{13}C NMR δ 11.6 (ethyl Me), 17.3 (ethyl CH_2), 28.0 (Me), 28.0 (Me), 38.2 (C-4), 50.3 (C-5), 144.3 (C-2), 165.3 (C-3), 208.5 (C-1).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.30.

2-Butyl-4,4-dimethyl-2-cyclopentenone (12b): colorless liquid (50%); IR C=O 1680 (s), C=C 1640 (w) cm^{-1}; ^1H NMR δ 0.90 (t, 3, J = 7 Hz, *n*-Bu Me), 1.20, 1.20 (s, 3 each, methyls), 1.2–1.6 (m, 4, methylenes), 2.13 (t, 2, J = 8 Hz, *n*-Bu C-1 Hs), 2.27 (s, 2, C-5 Hs), 7.03 (s, 1, H-3); ^{13}C NMR δ 13.7 (*n*-Bu Me), 22.3 (*n*-Bu C-3), 24.0 (*n*-Bu C-1), 28.3 (Me), 28.3 (Me), 29.7 (*n*-Bu C-2), 38.5 (C-4), 50.4 (C-5), 143.1 (C-2), 166.4 (C-3), 209.2 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.52; H, 10.83.

(*Z*)-2-Isobutylidene-4-ethylcyclopentanone (14b): colorless liquid (17%); IR C=O 1700 (s), C=C 1660 (s) cm^{-1}; ^1H NMR δ 0.92 (t, 3, J = 7 Hz, ethyl Me), 0.95, 0.95 (d, 3 each, J = 7 Hz, methyls), 1.2–1.5 (m, 3, CH, CH_2), 1.9–2.8 (m, 4, methylenes), 3.6–3.9 (m, 1, *i*-Bu CH), 5.6–5.8 (m, 1, olefinic H); ^{13}C NMR δ 11.9 (ethyl Me), 22.5 (Me), 22.7 (Me), 26.2 (*i*-Bu CH), 28.5 (ethyl CH_2), 36.0 (C-4), 38.0 (C-3), 47.1 (C-5), 133.5 (C-2), 147.3 (*i*-Bu C-1), 207.5 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.54; H, 10.85.

2-Isobutyl-4,4-dimethyl-2-cyclopentenone (12c): colorless liquid (45%); IR C=O 1687 (s), C=C 1625 (w) cm^{-1}; ^1H NMR δ 0.86, 0.86 (d, 3 each, J = 7 Hz, *i*-Bu methyls), 1.20, 1.20 (s, 3 each, methyls), 1.7–1.9 (m, 1, *i*-Bu CH), 2.01 (d, 2, J = 7 Hz, *i*-Bu CH_2), 2.26 (s, 2, C-5 Hs), 7.03 (s, 1, H-3); ^{13}C NMR δ 22.3 (*i*-Bu Me), 22.3 (*i*-Bu Me), 26.8 (*i*-Bu CH), 28.3 (Me), 28.3 (Me), 33.4 (*i*-Bu CH_2), 38.6 (C-4), 50.4 (C-5), 141.9 (C-2), 167.9 (C-3), 209.5 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.54; H, 10.83.

(*Z*)-2-Isobutylidene-4,4-dimethylcyclopentanone (15b): colorless liquid (15%); ^1H NMR δ 0.97, 0.97 (d, 3 each, J = 7 Hz, *i*-Bu methyls), 1.08, 1.08 (s, 3 each, methyls), 2.16 (s, 2, C-5 Hs), 2.38 (d, 2, J = 3 Hz, C-3 Hs), 3.6–3.8 (m, 1, CH), 5.61 (ddd, 1, J = 10, 3, 3 Hz, olefinic H); ^{13}C NMR δ 22.5 (*i*-Bu Me), 22.5 (*i*-Bu Me), 26.3 (CH), 28.2 (Me), 28.2 (Me), 33.6 (C-4), 46.4 (C-3), 55.5 (C-5), 133.8 (C-2), 148.0 (olefinic CH), 204.3 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.40; H, 10.99.

(*E*)-2-Isobutylidene-4-ethylcyclopentanone (16b): colorless liquid (97%); IR C=O 1720 (s), C=C 1640 (s) cm^{-1}; ^1H NMR δ 0.94 (t, 3, J = 6 Hz, ethyl Me), 1.04, 1.04 (d, 3 each, J = 7 Hz, methyls), 1.1–2.8 (m, 8, methylenes, methines), 6.39 (ddd, 1, J = 10, 3, 3 Hz, olefinic H); ^{13}C NMR δ 11.9 (ethyl Me), 21.6 (Me), 21.7 (Me), 28.9 (*i*-Bu CH), 29.0 (ethyl CH_2), 32.9 (C-3), 35.5 (C-4), 45.0 (C-5), 135.3 (C-2), 142.1 (olefinic CH), 207.0 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.36; H, 10.98.

(*E*)-2-Hexylidene-4,4-dimethylcyclopentanone (16c): colorless liquid (98%); IR C=O 1708 (s), C=C 1640 (s) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, *n*-Hex Me), 1.10, 1.10 (s, 3 each, methyls), 1.1–1.5 (m, 6, methylenes), 2.0–2.3 (m, 2, *n*-Hex allyl Hs), 2.18 (s, 2, C-5 Hs), 2.37 (s, 2, C-3 Hs), 6.5–6.7 (m, 1, olefinic H); ^{13}C NMR δ 13.8 (*n*-Hex Me), 22.4 (*n*-Hex C-5), 28.0 (*n*-Hex C-3), 28.6 (Me), 28.6 (Me), 29.5 (*n*-Hex C-2), 31.5 (*n*-Hex C-4), 33.7 (C-4), 41.9 (C-3), 53.6 (C-5), 135.0 (C-2), 136.6 (olefinic CH), 206.3 (C-1).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.26; H, 11.52.

(*E*)-Isobutylidene-4,4-dimethylcyclopentanone (16d): colorless liquid (97%); IR C=O 1705 (s), C=C 1638 (s) cm^{-1}; ^1H NMR δ 1.03, 1.03 (d, 3 each, J = 7 Hz, *i*-Bu methyls), 1.09, 1.09 (s, 3 each, methyls), 2.16 (s, 2, C-5 Hs), 2.3–2.6 (m, 1, *i*-Bu CH), 2.39 (d, 2, J = 3 Hz, C-3 Hs), 6.3–6.5 (m, 1, olefinic H); ^{13}C NMR δ 21.7 (*i*-Bu Me), 21.7 (*i*-Bu Me), 28.6 (Me), 28.6 (Me), 29.0 (*i*-Bu CH), 33.8 (C-4), 41.7 (C-3), 53.5 (C-5), 135.7 (C-2), 142.7 (olefinic CH), 207.0 (C-1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.59; H, 10.99.

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