A Convenient Method for the Preparation of (*Z*)-α,*β*-Unsaturated Carbonyl Compounds

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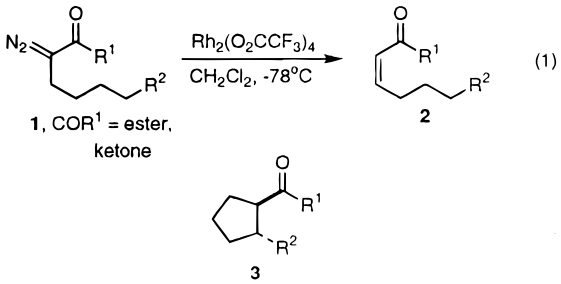
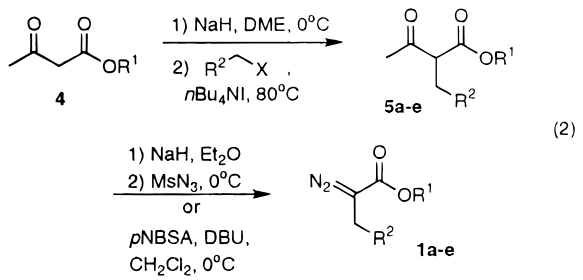
(*Z*)-α,*β*-Unsaturated carbonyl compounds **2** are important building blocks in organic synthesis.[2] Several procedures have been developed for the general synthesis of these compounds,[3] a few of which are known to exhibit substantial (*Z*)-selectivity (>90%).[4] Ganem has shown that α-diazo esters **1** undergo *β*-hydride elimination with rhodium(II) acetate to produce (*Z*)-enoates **2**,[5] but only in cases where no competing 1,5-insertion was possible (eq 1).[6,7] We have found that the more reactive rhodium (II) trifluoroacetate complex efficiently catalyzes the *β*-hydride elimination process, at low temperatures, without carbocycle (**3**) formation.



(1)

The starting α-diazo esters and α-diazo ketones can be prepared by direct diazo transfer, or by homologation of alkyl halides and tosylates. We used the latter approach to prepare the substrates listed in Table 1. Thus, α-alkylation of alkyl acetoacetates **4**[6a] with alkyl halides and tosylates produced α-substituted *β*-keto esters **5a**−**e**, which were converted to the α-diazo esters **1a**−**e** using one or the other of our established methods (eq 2).[8]



(2)

Subjection of the diazo precursors **1a**−**e** to rhodium-(II) trifluoroacetate dimer in CH_2Cl_2 at −78 °C for 1 h resulted in the selective formation of (*Z*)-α,*β*-unsaturated esters **2a**−**e** in good yields (Table 1). At most, only slight traces of the C-H 1,5-insertion products were detected in the crude mixtures.[9,10]

Subjection of the α-diazo ketone **1f**[8c] to the same conditions also resulted in the formation of (*Z*)-enone **2f**, without any trace of cyclization. This illustrates a new regioselective method for the construction of (*Z*)-α,*β*-unsaturated ketones.

The preference for elimination rather than cyclization under what are only slightly modified conditions is striking. With the very reactive rhodium tetrakis-(trifluoroacetate) catalyst, we speculate that the *enthalpy* of activation for these reactions is slight, allowing for *entropy* of activation to dominate. *β*-Hydride elimination (1,2-insertion), with a smaller entropy of activation, might then proceed more readily than 1,5-insertion, with a larger (more negative) entropy of activation.

This new method for constructing (*Z*)-α,*β*-unsaturated esters and ketones should be of general utility in organic synthesis. The excellent (>95%)[10] stereoselectivity is especially interesting.

Experimental Section[11]

Preparation of Methyl 2-Acetylundecanoate (5a). Sodium hydride (60% in mineral oil, 0.80 g, 20.0 mmol) was washed

(1) Undergraduate research participant.

(2) (a) Kelly, S. E. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; Vol. 1, p 729. (b) Boyd, G. V. In *The Chemistry of Enones*; John Wiley & Sons: New York, 1989; Pt. 1, p 281.

(3) For some general routes to α,*β*-unsaturated esters and ketones, see: (a) Addition/elimination reactions with selenium derivatives: (i) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. (ii) Reich, H. J.; Wollowitz, S. In *Organic Reactions*; John Wiley & Sons: New York, 1993; Vol. 44, p 1. (iii) Hooz, J.; Oudenes, J. *Synth. Commun.* **1980**, *10*, 667. (b) Addition/elimination reactions with sulfur derivatives: (i) Trost, B. M.; Salzmann, T. N. *J. Am. Chem. Soc.* **1973**, *95*, 6840. (ii) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887. (iii) Resek, J. E.; Meyers, A. I. *Tetrahedron Lett.* **1995**, *36*, 7051. (c) Condensation reactions with stabilized phosphonium ylides (review article): Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (d) The Horner−Wadsworth−Emmons reaction (review article): see ref 2a. (e) Carbonylations of vinylic halides: Urata, H.; Maekawa, H.; Shigeharu, T.; Fuchikami, T. *J. Org. Chem.* **1991**, *56*, 4320. (f) Carbonylations of vinylmercurials: Larock, R. C.; Narayanan, K. *J. Org. Chem.* **1984**, *49*, 3411.

(4) For (*Z*)-stereoselective syntheses of α,*β*-unsaturated esters: (a) With bis(trifluoroethyl)phosphonoesters: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405. (b) With trimethylphosphonium-propionates: Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 260. (c) With bis(phenyl)phosphonoesters: Ando, K. *Tetrahedron Lett.* **1995**, *36*, 4105. For (*Z*)-stereoselective syntheses of α,*β*-unsaturated ketones with stabilized ylides: (d) Pietrusiewicz, K. M.; Monkiewicz, J. *Tetrahedron Lett.* **1986**, *27*, 739. (e) Moorhoff, C. M.; Schneider, D. F. *Tetrahedron Lett.* **1987**, *28*, 4721. (f) McKenna, E. G.; Walker, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 568.

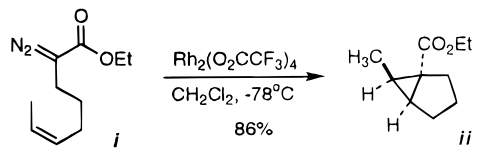
(5) Ikota, N.; Takamura, N.; Young, S. D.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 4163.

(6) *β*-Hydride elimination has been shown to be competetive with rhodium-catalyzed 1,5-insertion reactions: (a) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436. (b) Hennessy, M. J. Ph.D. Dissertation, The University of Delaware, 1989. (c) Galeazzi, E.; Guzman, A.; Pinedo, A.; Saldana, A.; Torre, D.; Muchowski, J. M. *Can. J. Chem.* **1983**, *61*, 454.

(7) (a) A rhodium(II) acetate-catalyzed method for the elimination of α-diazo *β*-methoxy ketones to (*E*)-*β*-methoxy enones has also been reported: Hudlicky, T.; Olivo, H. F.; Natchus, M. G.; Umpierrez, E. F.; Pandolfi, E.; Volonterio, C. *J. Org. Chem.* **1990**, *55*, 4767. (b) It has also been shown that $AgNO_3$-promoted decomposition of acyldiazoethanes can be used to prepare enones: Duggleby, P. McC.; Holt, G.; Hope, M. A.; Lewis, A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 3020.

(8) (a) Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077. (b) Taber, D. F.; You, K.; Song, Y. *J. Org. Chem.* **1995**, *60*, 1093. (c) Taber, D. F.; Gleave, D. M.; Herr, R. J.; Moody, K.; Hennessy, M. J. *J. Org. Chem.* **1995**, *60*, 2283.

(9) However, subjection of the α-diazo ester ***i*** to the same conditions resulted in exclusive C−C insertion product ***ii***.

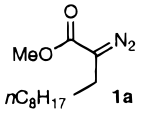
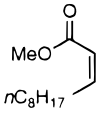
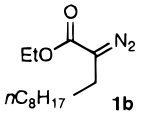
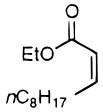
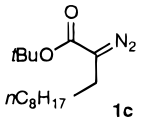
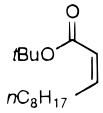
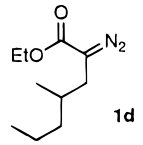
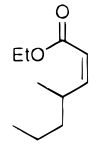
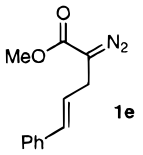
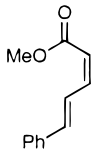
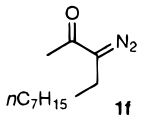
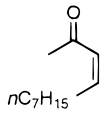


(10) All unsaturated products (**2a-f**) were clean by ^1H and ^{13}C NMR spectroscopy, showing no trace of the (*E*)-isomer in the crude product mixture before chromatography. Early reactions run at higher temperatures showed significant contamination by the (*E*)-isomer.

(11) For a summary of general experimental procedures see: Taber, D. F.; Houze, J. B. *J. Org. Chem.* **1994**, *59*, 4004.

0022-3263/96/1961-2908$12.00/0

Table 1. β-Hydride Elimination of α-Diazo Carbonyl Compounds 1

Entry	α-Diazocarbonyl Compound	α,β-Unsaturated Carbonyl Compound	Yield
1	 **1a**	 **2a**	80%
2	 **1b**	 **2b**	85%
3	 **1c**	 **2c**	91%
4	 **1d**	 **2d**	82%
5	 **1e**	 **2e**	94%
6	 **1f**	 **2f**	92%

three times with petroleum ether and then suspended in 10 mL of dry DME and cooled to 0 °C under nitrogen. Methyl acetoacetate (2.16 mL, 20.0 mmol) was added dropwise to give a solid mass. nBu$_4$NI (0.21 g, 1.0 mmol) was added, followed by 1-bromononane (1.91 mL, 10.0 mmol), and the reaction was stirred at 80 °C for 20 h. The mixture was cooled to rt, diluted with 10 mL of 5% aqueous HCl and extracted three times with 20 mL of petroleum ether. The combined organic extracts were dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed to give the α-alkylated β-keto ester **5a** as a colorless oil (1.99 g, 82%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.73; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.33 (t, 1H, J = 7.4 Hz), 2.11 (s, 3H), 1.71 (m, 2H), 1.15 (m, 14 H), 0.77 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 202.8, 170.1, 31.6, 29.1 (× 2), 28.0 (× 2), 27.2 (× 2), 22.4; down: 59.4, 52.0, 28.4, 13.8; IR (film) 2924, 2855, 1746, 1721, 1645, 1435, 1358, 1152 cm^{-1}; EI MS m/z (rel intensity) 242 (M^+, 1), 200 (7), 157 (6), 129 (11), 116 (60), 87 (100), 74 (23), 59 (12).

Ethyl 2-Acetylundecanoate (5b). From 1.00 mL of 1-bromononane was obtained the β-keto ester **5b** as a colorless oil (1.16 g, 86%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.54; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.19 (q, 2H, J = 7.2 Hz), 3.40 (t, 1H, J = 7.5 Hz), 2.22 (s, 3H), 1.82 (m, 2H), 1.25 (m, 15H), 0.87 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 203.2, 169.8, 61.1, 31.8, 29.4, 29.2, 28.1, 27.3, 22.6; down: 59.8, 28.6, 14.0; IR (film) 2926, 2855, 1743, 1718, 1644, 1466, 1358, 1242, 1151, 1120 cm^{-1}; EI MS m/z (rel intensity) 257 (M^+, 3), 214 (32), 171 (12), 157 (16), 143 (23), 130 (97), 101 (100), 72 (66); HRMS (calcd for $C_{15}H_{28}O_3$) 256.2038, found 256.2058.

***tert*-Butyl 2-Acetylundecanoate (5c).** From 4.78 mL of 1-bromononane was obtained the β-keto ester **5c** as a colorless oil (5.11 g, 72%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.69; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.21 (t, 1H, J = 7.4 Hz), 2.12 (s, 3H), 1.67 (m, 2H), 1.38 (s, 9H), 1.17 (m, 12H), 0.79 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 203.0, 168.5, 81.0, 31.2, 28.9, 28.7 (× 2), 28.6, 27.5, 26.7, 22.0; down: 60.4, 27.9, 27.3 (× 3), 13.4; IR (film) 2925, 2855, 1714, 1641, 1460, 1368, 1250, 1148, 848 cm^{-1}; EI MS m/z (rel intensity) 211 (M^+ − tBuO, 1), 158 (1), 112 (3), 103 (13), 102 (15), 98 (16), 57 (100).

Ethyl 2-Acetyl-4-methylheptanoate (5d). From 1.67 g of 2-methylpentanyl iodide was obtained an inseparable mixture of β-keto ester diastereomers **5d** as a colorless oil (1.31 g, 78%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.49; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.17 (q, 2H, J = 7.2 Hz), 3.47 (dd, 1H, J = 5.2, 7.9 Hz), 2.18 (s, 3H), 1.85 (m, 1H), 1.66 (m, 1H), 1.28 (m, 4H), 1.23 (t, 3H, J = 7.2 Hz), 1.07 (m, 1H), 0.84 (d, 6H, J = 6.4 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 203.3, 170.0, 61.2, 39.2, 35.3, 19.8; down: 58.1, 30.6, 28.5, 19.3, 14.1, 14.0; IR (film) 2959, 2874, 1746, 1715, 1464, 1359, 1242, 1183, 1025 cm^{-1}; EI MS m/z (rel intensity) 215 (M^+ + 1, 1), 172 (26), 143 (17), 131 (22), 130 (67), 115 (41), 101 (100), 97 (15), 84 (14), 73 (77); HRMS (calcd for $C_{12}H_{23}O_3$) 215.1647, found 215.1652.

Methyl (*E*)-2-Acetyl-5-phenylpentanoate (5e). From 3.00 g of cinnamyl bromide was obtained the β-keto ester **5e** as a colorless oil (3.29 g, 93%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.49; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.46 (d, 1H, J = 15.8 Hz), 6.12 (dt, 1H, J = 7.1, 15.8 Hz), 3.74 (s, 3H), 3.62 (t, 1H, J = 7.4 Hz), 2.76 (t, 2H, J = 7.3 Hz), 2.26 (s, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 202.1, 169.6, 136.9, 31.5; down: 132.7, 128.4 (× 2), 127.3, 126.1 (× 2), 125.6, 57.3, 52.3, 29.2; IR (film) 2926, 2855, 1743, 1718, 1644, 1466, 1358, 1242, 1151, 1120 cm^{-1}; EI MS m/z (rel intensity) 232 (M^+, 34), 190 (26), 189 (51), 168 (33), 156 (100), 131 (54), 130 (39), 119 (69), 116 (56), 104 (18), 91 (88), 77 (18); HRMS (calcd for $C_{14}H_{16}O_3$) 232.1099, found 232.1082.

Preparation of Methyl 2-Diazoundecanoate (1a). Method A: Sodium hydride (60% in mineral oil, 0.151 g, 3.78 mmol) was washed three times with petroleum ether and then suspended in 10 mL of dry diethyl ether at 0 °C under nitrogen. To this solution was then added dropwise 0.611 g (2.52 mmol) of β-keto ester **5a** in 3 mL of diethyl ether. After the mixture had stirred for 10 min, 0.915 g (7.56 mmol) of methanesulfonyl azide was added dropwise, and the mixture was allowed to warm to rt over 5 h. The mixture was then diluted with 10 mL of 10% aqueous NaOH and extracted three times with 25 mL of ethyl acetate. The organic layers were then washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed to give the α-diazo ester **1a** as a yellow oil (0.531 g, 93%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.83; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.22 (t, 2H, J = 7.0 Hz), 1.42 (m, 2H), 1.19 (m, 12H), 0.80 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 167.9, 31.8, 29.4, 29.1, 28.6, 27.5, 23.0 (× 2), 22.6; down: 51.6, 13.9; IR (film) 2926, 2855, 2360, 2079, 1699, 1436, 1351, 1136, 739 cm^{-1}; EI MS m/z (rel intensity) 199 (M^+ − N_2, 2), 167 (6), 137 (2), 124 (8), 113 (100), 100 (30), 87 (43), 81 (60), 69 (37).

Ethyl 2-Diazoundecanoate (1b). Method A: From 1.284 g of β-keto ester **5b** was obtained the α-diazo ester **1b** as a yellow oil (0.915 g, 76%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.88; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.14 (q, 2H, J = 7.1 Hz), 2.22 (t, 2H, J = 7.1 Hz), 1.43 (m, 2H), 1.20 (m, 15H), 0.81 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 167.6, 60.6, 31.8, 29.4, 29.2 (× 2), 28.7, 27.5, 22.9, 22.6; down: 14.4, 14.0; IR (film) 2928, 2856, 2084, 1699, 1465, 1371, 1304, 1134, 739 cm^{-1}; EI MS m/z (rel intensity) 167 (M^+ − N_2, − OEt, 2), 127 (13), 99 (32), 88 (22), 81 (23), 69 (23), 55 (100).

***tert*-Butyl 2-Diazoundecanoate (1c).** Method A: From 0.658 g of β-keto ester **5c** was obtained the α-diazo ester **1c** as a yellow oil (0.452 g, 73%). TLC R_f (5% ethyl acetate/petroleum ether) = 0.77; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.22 (t, 2H, J = 7.0 Hz), 1.45 (s, 9H), 1.24 (m, 14H, 0.85 (m, 3H); IR (film) 3428, 2957, 2856, 2078, 1694, 1456, 1368, 1133 cm^{-1}; EI MS m/z (rel intensity) 167 (M^+ − N_2, − tBuO, 6), 124 (5), 111 (2), 101 (3), 99 (24), 81 (11), 73 (7), 57 (100).

Ethyl 2-Diazo-4-methylheptanoate (1d). Method B: To a solution of the β-keto ester **5d** (1.14 g, 5.3 mmol) and *p*-nitrobenzenesulfonyl azide (2.43 g, 10.6 mmol) in 30 mL of dry CH_2Cl_2 under nitrogen at 0 °C was added dropwise DBU (1.6 mL, 10.6 mmol). The mixture was stirred for 90 min, after which 30 mL of 10% NaOH soln was added, and the mixture was warmed to rt. The crude α-diazo ester was extracted three times with CH_2Cl_2, washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed to provide the α-diazo ester **1d** as a yellow oil (0.83 g, 79%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.75; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.22 (q, 2H, J = 7.2 Hz), 2.19 (ddd, 2H, J = 6.1, 14.9, 36.9 Hz), 2.10 (m, 1H), 1.31 (m, 4H), 1.27 (t, 3H, J = 7.2 Hz), 0.92 (d, 6H, J = 6.7 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 60.7, 38.4, 30.6, 20.0;

down: 32.4, 19.1, 14,2 (× 2); IR (film) 2959, 2873, 2361, 2080, 1697, 1371, 1323, 1136 cm^{-1}; EI MS *m/z* (rel intensity) 170 ($M^+ - N_2$, 4), 155 (2), 141 (30), 125 (90), 113 (68), 96 (75), 82 (14), 55 (100).

Methyl (*E*)-2-Diazo-5-phenylpentanoate (1e). Method B: From 1.86 g of *β*-keto ester **5e** was obtained the α-diazo ester **1e** as a yellow oil (1.44 g, 83%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.32; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36 (m, 5H), 6.49 (d, 1H, J = 15.8 Hz), 6.21 (dt, 1H, J = 6.8, 15.8 Hz), 3.80 (s, 3H), 3.22 (d, 2H, J = 6.8 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 167.2, 136.5, 26.6; down: 132.6, 128.4 (× 2), 127.4, 126.1 (× 2), 123.8, 51.8; IR (film) 3028, 2952, 2080, 1694, 1598, 1496, 1436, 1337, 1190, 1115, 967, 913, 739, 695 cm^{-1}; EI MS *m/z* (rel intensity) 188 ($M^+ - N_2$, 14), 157 (16), 129 (100), 128 (88), 117 (6), 102 (17), 77 (22), 64 (18), 51 (28).

Preparation of Methyl (*Z*)-2-Undecenoate (2a). To a solution of the α-diazo ester **1a** (0.208 g, 0.92 mmol) in 20 mL of dry CH_2Cl_2 at −78 °C under nitrogen was added dropwise a solution of rhodium tetrakis(trifluoroacetic acid) dimer (0.0060 g, 0.01 mmol) in 0.5 mL of dry CH_2Cl_2 (precooled to 0 °C). The mixture was stirred for 1 h, concentrated *in vacuo*, and immediately chromatographed to provide the (*Z*)-α,*β*-unsaturated ester **2a** as a colorless oil (0.182 g, 80%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.85; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.14 (dt, 1H, J = 7.5, 11.5 Hz), 5.68 (d, 1H, J = 11.5 Hz), 3.61 (s, 3H), 2.57 (dq, 2H, J = 1.4, 7.4 Hz), 1.35 (m, 2H), 1.18 (m, 10H), 0.80 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 166.5, 31.7, 29.3, 29.3, 29.1, 28.9, 28.8, 22.5; down: 150.7, 119.0, 50.6, 13.9; IR (film) 2926, 2856, 1728, 1645, 1436, 1197, 1175, 819 cm^{-1}; EI MS *m/z* (rel intensity) 199 (M^+, 2), 167 (7), 124 (9), 113 (100), 100 (33), 87 (47), 74 (43); HRMS (calcd for $C_{12}H_{22}O_2$) 198.1620, found 198.1613.

Ethyl (*Z*)-2-Undecenoate (2b). From 0.401 g of α-diazo ester **1b** was obtained the (*Z*)-α,*β*-unsaturated ester **2b** as a colorless oil (0.301, 85%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.93; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.14 (m, 1H)), 5.68 (d, 1H, J = 11.5 Hz), 4.08 (q, 2H, J = 7.2 Hz), 2.00 (q, 2H, J = 7.2 Hz), 1.36 (m, 2H), 1.21 (m, 13H), 0.80 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 166.3, 59.6, 31.8, 29.3, 29.2, 29.1, 29.0, 28.9, 22.6; down: 150.4, 119.6, 14.2, 14.0; IR (film) 2108, 1722, 1644, 1465, 1134 cm^{-1}; EI MS *m/z* (rel intensity) 212 (M^+, 5), 167 (17), 127 (100), 115 (47), 101 (32), 99 (39), 88 (48), 84 (20); HRMS (calcd for $C_{13}H_{24}O_2$) 212.1776, found 212.1761. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54%; H, 11.39%. Found: C, 73.47%; H, 11.25%.

***tert*-Butyl (*Z*)-2-Undecenoate (2c).** From 0.436 g of α-diazo ester **1c** was obtained the (*Z*)-α,*β*-unsaturated ester **2c** as a colorless oil (0.353, 91%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.90; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.09 (m, 1H), 5.64 (d, 1H, J = 11.5 Hz), 2.58 (q, 2H, J = 7.2 Hz), 1.47 (s, 9H), 1.25 (m, 12H0, 0.86 (m, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 167.0, 80.8, 31.8, 29.4, 29.2, 28.7, 27.5, 22.9, 22.6; down: 148.9, 121.4, 28.3 (× 3), 14.0; IR (film) 2958, 2928, 2856, 2361, 1716, 1641, 1367, 1215, 1152, 820 cm^{-1}; FAB MS *m/z* (rel intensity) 241 ($M^+ + 1$, 15), 221 (30), 207 (24), 185 (100), 167 (37), 147 (61); HRMS (calcd for $C_{15}H_{29}O_2$) 241.2168, found 241.2171.

Ethyl (*Z*)-4-Methyl-2-heptenoate (2d). From 0.2290 g of α-diazo ester **1d** was obtained the (*Z*)-α,*β*-unsaturated ester **2d** as a colorless oil (0.1612, 82%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.79; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.92 (dd, 1H, J = 10.2, 11.5 Hz), 5.68 (d, 1H, J = 11.5 Hz), 4.15 (q, 2H, J = 7.2 Hz), 3.50 (m, 1H), 1.27 (t, 3H, J = 7.1 Hz), 1.27 (m, 4H), 0.99 (d, 3H, J = 6.6 Hz), 0.88 (t, 3H, J = 7.2Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 166.4, 59.7, 39.2, 20.7; down: 156.0, 118.2, 32.4, 20.2, 14.2, 14.1; IR (film) 2960, 2931, 1722, 1646, 1457, 1417, 1186, 1035, 824 cm^{-1}; EI MS *m/z* (rel intensity) 170 (M^+, 2), 141 (5), 125 (7), 113 (15), 95 (19), 83 (11), 82 (19), 71 (11), 67 (26), 55 (100).

Methyl (*Z*,*E*)-5-Phenyl-2-pentenoate (2e). From 0.1610 g of α-diazo ester **1e** was obtained the (*Z*)-α,*β*-unsaturated ester **2e** as a colorless oil (0.1315, 94%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.58; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.16 (dd, 1H, J = 12.4, 16.7 Hz), 7.54 (d, 2H, J = 8.1 Hz), 7.34 (m, 3H), 6.77 (q, 2H, J = 15.7 Hz), 5.74 (d, 1H, J = 11.2 Hz), 3.77 (s, 3H); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 166.8, 136.2; down: 144.9, 141.3, 128.9, 128.6 (× 2), 127.4 (× 2), 124.8, 116.9, 51.1; IR (film) 3024, 2949, 2071, 1712, 1625, 1450, 1392, 1172, 1000, 959, 820 cm^{-1}; EI MS *m/z* (rel intensity) 188 (M^+, 8), 157 (10), 129 (96), 128 (100), 115 (15), 102 (25), 77 (38), 63 (34), 51 (87); HRMS (calcd for $C_{12}H_{12}O_2$) 188.0837, found 188.0829.

(*Z*)-3-Undecen-2-one (2f). From 0.0960 g of α-diazo ketone **1f**[8c] was obtained the (*Z*)-α,*β*-unsaturated ketone **2f** as a colorless oil (0.0757, 92%). TLC R_f (10% ethyl acetate/petroleum ether) = 0.74; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.10 (m, 2H, J = 11.7 Hz), 2.59 (q, 2H, J = 7.1 Hz), 2.19 (s, 3H), 1.39 (m, 2H), 1.26 (m, 8H), 0.86 (t, 3H, J = 5.3 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ up: 199.3, 31.7, 29.3, 29.2, 29.1 (× 2), 29.0; down: 148.8, 127.0, 31.5, 14.0; IR (film) 2926, 2856, 2361, 1696, 1616, 1558, 1457, 1418, 1355, 1178 cm^{-1}; EI MS *m/z* (rel intensity) 168 (M^+, 2), 153 (2), 125 (3), 110 (10), 97 (100), 84 (21), 71 (19), 69 (43), 55 (44); HRMS (calcd for $C_{11}H_{20}O$) 168.1514, found 168.1517.

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Supporting Information Available: ^{1}H and ^{13}C spectra for compounds **1a**−**e**, **2a**−**f**, and **5a**−**e** (31 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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