in toluene (50 mL). The mixture was refluxed for 2.5 h. After cooling to room temperature, the reaction mixture was filtered through Celite pad into *tert*-butyl alcohol (10 mL) under nitrogen atmosphere. Concentration of the filtrate and column chromatography gave **36** (300 mg, 50%) as a white solid. It was recrystallized from methanol: mp 150 °C; IR (KBr) ν_{max} 3060, 1735 (carbonyl), 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 0.9 (q, 1 H, J = 12 Hz), 2.0–3.0 (m, 11 H), 3.1–3.5 (m, 2 H), 5.4 (m, 1 H), 5.8 (m, 1 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 220.9 (s), 219.3 (s), 132.6 (d), 131.7 (d), 77.7 (s), 63.0 (d), 58.7 (d), 54.1 (d), 53.8 (d), 45.2 (t), 44.5 (t), 41.2 (d, 2 C), 40.8 (t), 39.5 (t); mass spectrum (70 eV) m/e (relative intensity) 228 (molecular ion, 100), 210 (14), 200 (13), 160 (26), 147 (25), 132 (35), 130 (32), 121 (42), 105 (97), 91 (34). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 6.80.

6-Methoxypentacyclo[10.2.1.0^{4,8}.0^{4,10}.0^{9,13}]pentadecane-3,10-dione (37). Dione **35**[14] (1.2 g, 4.65 mmol) was treated with 1.2 g of Na–K alloy (prepared from 200 mg of sodium and 1.0 g of potassium as described earlier) and trimethylchlorosilane (10 mL) in 100 mL of dry toluene. The mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad into *tert*-butyl alcohol (10 mL) under nitrogen atmosphere. Concentration of the filtrate and column chromatography gave **37** (720 mg, 60%) as a white solid. It was recrystallized from pet ether–carbon tetrachloride: mp 97–98 °C; IR (KBr) ν_{max} 1730 cm^{-1} (carbonyl); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 0.8 (q, 1 H, J = 12 Hz), 1.4–3.0 (m, 13 H), 3.2 (s, 3 H, OCH_3), 3.3–3.8 (m, 3 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 222.8 (s), 220.4 (s), 87.3 (d, $HCOCH_3$), 72.5 (s), 62.1 (d), 57.7 (q, OCH_3), 55.9, 54.9, 53.8, 45.9 (t), 44.9 (t), 41.0 (d, 2 C), 39.3 (d), 30.7 (t), 30.6 (t); mass spectrum (70 eV) m/e (relative intensity) 260 (molecular ion, 54), 245 (19), 232 (30), 228 (46), 189 (95), 161 (6), 117 (22), 105 (25), 91 (43), 79 (23), 72 (100). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.74; H, 7.56.

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2-Alkenyl-Substituted Methyl 2-Siloxycyclopropanecarboxylates as Masked Vinyl Ketones: Efficient Syntheses of Highly Functionalized Michael Adducts

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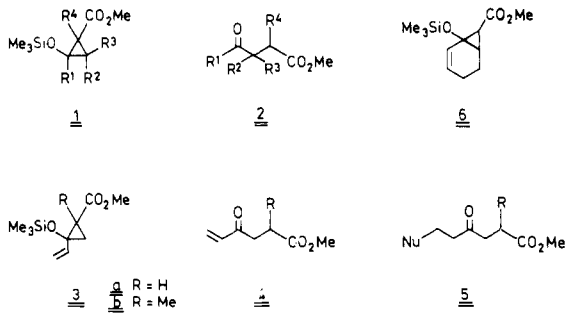
2-Alkenyl-substituted methyl 2-siloxycyclopropanecarboxylates **3a**, **3b**, and **6**—easily available from the corresponding silyl enol ether—react with a variety of O-, N-, S-, and C-nucleophiles under mild acidic or basic conditions providing polyfunctionalized products **7–19** in good to excellent yields via 1,4-addition to vinyl ketones formed in situ. Due to the versatility of the nitro group, nitroalkane adducts **15–19** are of special interest for further transformations.

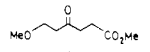
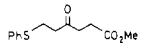
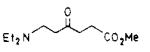
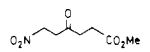
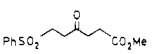
Michael addition of nucleophiles toward α,β-unsaturated carbonyl compounds is a key reaction to construct polyfunctional carbon skeletons.[1] Numerous examples demonstrate the utility of this basic step in synthetic strategy.

We have shown that the easily available[2] methyl 2-siloxycyclopropanecarboxylates **1** are versatile intermediates for the high-yield synthesis of several 4-oxoalkanoate derivatives (e.g., **2**).[3] If R^1 is an alkenyl group as in **3** these



cyclopropanes are masked vinyl ketones since **4** can be liberated by ring opening with fluoride or acid.[3a] We therefore looked for efficient one-pot procedures allowing generation of 4-type acceptors and trapping of these intermediates with nucleophiles. This straightforward

Table I. Conversion of Vinylcyclopropane 3a to 6-Heterosubstituted 4-Oxoalkanoates 7–11

entry	nucleophile	solvent	"catalyst"	product	yield
a	MeOH	MeOH	K_2CO_3	 7	91 %
b	PhSH	–	Triton B	 8	69 %[a]
c	Et_2NH	THF	$NEt_3 \cdot 3HF$	 9	98 %
d	$NaNO_2$	THF	AcOH	 10	55 %
e	$NaSO_2Ph$	CH_2Cl_2/H_2O	HCl	 11	54 %

[a] This material contains traces of Ph_2S_2 which can be removed by chromatography. Participation of a free radical path forming **8** cannot be excluded.

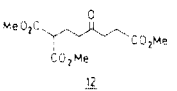
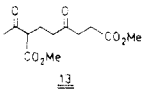
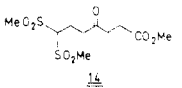
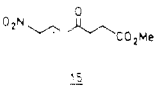
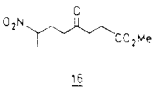
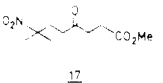
(1) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React. (N.Y.)* **1959**, *10*, 179. House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: Menlo Park, 1972. Warren, S. "Organic Synthesis: The Disconnection Approach"; John Wiley & Sons: Chichester, 1982. Fuhrhop, J.; Penzlin, G. "Organic Synthesis"; Verlag Chemie: Weinheim, 1983.

(2) (a) Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 512. (b) Reichelt, I., Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 531.

(3) (a) Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 802. (b) Grimm, E. L.; Reissig, H.-U. *J. Org. Chem.* **1985**, *50*, 242 and references cited therein.

0022-3263/85/1950-5543$01.50/0

Table II. Addition of C-Nucleophiles to Vinylcyclopropane 3a "Catalyzed" by Triton B at 70 °C

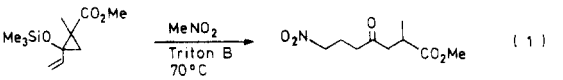
entry	nucleophile	product	yield
a	$(MeO_2C)_2CH_2$	 12	62 %
b	MeO_2CCH_2COMe	 13	62 %
c	$(MeO_2S)_2CH_2$ (solvent THF)	 14	39 %
d	$MeNO_2$	 15	75 %
e	$EtNO_2$	 16	91 %
f	Me_2CHNO_2	 17	55 %

pathway would lead to 6- or 7-functionalized 4-oxoalkanoates **5**.

Starting Materials. As with cyclopropanes **1**,[2a] vinylcyclopropane **3a** can be synthesized effectively in 100-mmol scale by adding methyl diazoacetate (1.1 equiv) to 2-(trimethylsiloxy)buta-1,3-diene[4] under $Cu(acac)_2$ catalysis. These semioptimized conditions lead to an improved 73% yield. Use of $Rh_2(OAc)_4$ gives inferior results.[5] Similarly the bicyclic system **6** is obtained from the corresponding 2-(trimethylsiloxy)cyclohexa-1,3-diene[6] in good yield (65%). Deprotonation/alkylation[2b] of **3a** delivers **3b** (81%).

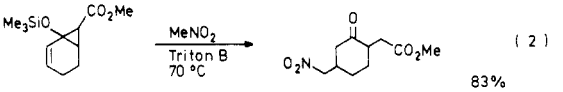
Addition of Heteronucleophiles. Reactions of several characteristic heteronucleophiles with **3a** were examined first. Table I demonstrates that O-, N-, as well as S-nucleophiles add to the vinyl ketone **4a** generated from **3a** in situ under mild basic (entries a, b) or acid (entries c, d, e) conditions, delivering 6-heterosubstituted 4-oxoalkanoates **7–11** in good to excellent yields.

Addition of Carbon Nucleophiles. More interestingly, addition of a variety of CH-acidic compounds toward **4a**—generated from **3a** by action of the catalyst Triton B (0.08 equiv, 40% in MeOH)—smoothly affords the Michael adducts **12–17** in very good yields (Table II). Under these reaction conditions methoxide very likely acts as the desilylating agent[3a] as well as a base forming the corresponding carbanions. Other catalysts (e.g., benzyltrimethylammonium fluoride, $KF{\cdot}2H_2O$/benzyltrimethylammonium chloride) are less effective. Two equivalents of the CH-acidic component are employed in entries a–c, whereas nitroalkanes (entries d–f) are used in larger excess (40–70 equiv). However, **16** can also be synthesized in satisfying yield (51%) by reducing the excess of nitroethane to 1 equiv. Further examples shown in eq 1 and 2 demonstrate that other vinylcyclopropanes can serve as vinyl ketone precursors with comparable efficiency. As expected **19** is formed as a mixture of stereoisomers with



(1)

18 67 %



(2)

83 %

19 (trans : cis = 87:13)

the thermodynamically more stable trans compound dominating.

Conclusions. Alkenyl-substituted cyclopropanes like **3a**, **3b**, and **6** allow efficient preparation of Michael adducts **7–19** with considerable structural variations of the employed nucleophile. Due to the availability of the cyclopropanes and the simplicity of the procedures these methods will allow synthesis of Michael adducts even in moderate to large scale. Polyfunctionalized products **7–19** could be versatile starting materials for further useful reactions, e.g., conversion into carbo- and heterocycles. Nitroalkane adducts should be of special value since the nitrogroup can be transformed to several other functions.[7] Nef reaction, for instance, would generate carbonyl groups, therefore, adducts **15**, **16**, **18**, and **19** can be regarded as compounds with three differentiated carbonyl functions having a 1,4,7-heteroatom pattern. Their synthesis can be analyzed in terms of two umpolung steps, the first by applying the cyclopropane trick, the second by making use of the nitronate anion/acyl anion equivalence.[8] Compounds like **16** should serve as easily available precursors for the shortcut preparation of certain macrolide blocks. Research along these lines will be reported in due time.

Experimental Section

For general remarks see ref 3b and 2a. IR spectra are recorded in CCl_4, NMR spectra in $CDCl_3$. Triton B (benzyltrimethylammonium hydroxide) is used as 40% methanolic solution.

Synthesis of 3a. According to the general procedure in ref 2a, 14.2 g (100 mmol) of 2-(trimethylsiloxy)buta-1,3-diene,[4] 11.0 g (110 mmol) of methyl diazoacetate, and 373 mg (1.72 mmol) of copper(II) pentanedionate in 120 mL of benzene afford after filtration and distillation (bp 48–51 °C (1 mm)) 15.6 g (73%) of **3a** as colorless liquid, which crystallizes in part at 4 °C. For analytical and spectroscopic data, see ref 2a.

Methyl 1-(Trimethylsiloxy)bicyclo[4.1.0]hept-2-ene-7-carboxylate (6). According to the general procedure in ref 2a, 11.8 g (70.0 mmol) of 2-(trimethylsiloxy)cyclohexa-1,3-diene,[6] 7.51 g (75.0 mmol) of methyl diazoacetate, and 363 mg of $Cu(acac)_2$ in 75 mL of benzene afford after filtration and distillation (bp 88–91 °C (0.8 mm)) 10.9 g (65%) of **6** as a colorless liquid (cis:trans = 64:36): ^1H NMR δ 0.23 (s, 9 H, $OSiMe_3$), 2.5–1.6 (m, 6 H), 3.63, 3.68 (2 s, 3 H, CO_2Me), 6.3–5.3 (m, 2 H, vinyl-H); IR 1735 (CO_2Me), 1640 (C=C). Anal. Calcd for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.38. Found: C, 59.73; H, 8.79.

Synthesis of 3b. According to the general procedure in ref 2b, 2.14 g (10.0 mmol) of **3a**, 15 mmol of lithium diisopropylamide, and 3.62 g (25 mmol) of methyl iodide (16 h, −78 °C) provide after aqueous workup and distillation (bp 95 °C (1 mm)) 1.84 g (81%) of **3b** as a colorless liquid. For analytical and spectroscopic data, see ref 2b.

Methyl 6-Methoxy-4-oxohexanecarboxylate (7). **3a** (2.14 g, 10.0 mmol) is dissolved in 10 mL of CH_3OH and mixed with 20 mg of K_2CO_3 at 5 °C. After stirring for 16 h at room temperature, filtration and distillation (bp 80 °C (0.08 mm)) gives

(4) Cazeau, P.; Moulines, R.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C9.
(5) Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H.; Buhro, W. E. *Tetrahedron Lett.* **1982**, *23*, 2261.
(6) Girad, C.; Conia, J. M. *J. Chem. Res., Miniprint* **1978**, 2351; *J. Chem. Res., Synop.* **1978**, 182.
(7) Reviews; (a) Schwarz, H. H.; Apel, G. "Methoden der Organischen Chemie"; Houben-Weyl-Müller, Ed.; Thieme: Stuttgart 1971; Vol. X/1. (b) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1.
(8) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

1.59 g (91%) of **7** as a colorless liquid:[9] ^{1}H NMR δ 2.3–2.9 (m, 6 H), 3.25, 3.60 (2 s, 3 H, 3 H, OMe, CO_2Me), 3.58 (t, J = 6 Hz, 2 H, OCH_2); IR 1740 (CO_2Me), 1720 (C=O).

Methyl 4-Oxo-6-(phenylthio)hexanoate (8). 3a (1.07 g, 5.00 mmol), freshly distilled thiophenol (1.10 g, 10.0 mmol), and 0.125 mL of a Triton B solution are treated under N_2 for 4 h at 70 °C. After evaporation of excess thiophenol the residue is dissolved in CH_2Cl_2 washed with 2 N HCl, saturated $NaHCO_3$, and brine dried with $MgSO_4$, concentrated, and distilled (bp 140 °C (0.02 mm)), giving 864 mg (69%) of **8** which contains traces of diphenyl disulfide. The analytical sample was obtained by chromatography: ^{1}H NMR δ 2.4–3.2 (m, 8 H), 3.56 (s, 3 H, CO_2Me), 7.43 (s, 5 H, C_6H_5); IR 1745 (CO_2Me), 1710 (CO). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 62.28; H, 6.63.

Methyl 6-(Diethylamino)-4-oxohexanoate (9). 3a (1.07 g, 5.00 mmol), 15 mL of diethylamine, and 15 mL of THF are stirred with $NEt_3 \cdot 3HF$[10] (1.61 g, 5.00 mmol) for 16 h at room temperature. Addition of 50 mL of water, extraction with ether, drying with $MgSO_4$, and distillation (bp 95 °C (0.02 mm)) yields 1.05 g (98%) **9**: ^{1}H NMR δ 0.78 (t, J = 7 Hz, 6 H), 2.0–2.8 (m, 12 H), 3.45 (s, 3 H, CO_2Me); IR 1750 (CO_2Me), 1725 (C=O). Anal. Calcd for $C_{11}H_{21}NO_3$: C, 61.37; H, 9.83; N, 6.51. Found: C, 61.75; H, 10.07; N, 6.59.

Methyl 6-Nitro-4-oxohexanoate (10). 3a (1.07 g, 5.00 mmol), acetic acid (1.50 g, 25.0 mmol), and $NaNO_2$ (1.75 g, 25.0 mmol) are stirred in 5 mL of THF for 48 h at room temperature. Addition of 20 mL of water, extraction with ethyl acetate, washing of the organic phase with saturated $NaHCO_3$ and brine, drying with Na_2SO_4, and concentration results in 851 mg of crude product, which contains **4a** and unknown impurities. Chromatography (SiO_2, petroleum ether/ethyl acetate, 1:1) affords 516 mg (55%) of pure **10**: ^{1}H NMR δ 2.4–3.0 (m, 4 H), 3.10 (t, J = 7 Hz, 2 H, CH_2), 3.60 (s, 3 H, CO_2Me), 4.60 (t, J = 7 Hz, 2 H, CH_2NO_2); IR 1740 (CO_2Me), 1730 (C=O), 1360 (NO_2). Distillation (bp 120 °C (0.02 mm)) gives the analytical sample. Anal. Calcd for $C_7H_{11}NO_5$: C, 44.44; H, 5.86; N, 7.40. Found: C, 44.67; H, 5.86; N, 7.40.

Methyl 4-Oxo-6-(phenylsulfonyl)hexanoate (11). 3a (1.07 g, 5.00 mmol), 15 mL of CH_2Cl_2, and $C_6H_5SO_2Na$ (1.64 g, 10.0 mmol) in 20 mL of water are combined and stirred with 10 mL of 2 N HCl for 19 h at room temperature. After extraction with CH_2Cl_2, washing of the organic phase with 2 N NaOH, 2 N HCl, and brine, drying with $MgSO_4$, and concentration in vacuo, 760 mg (54%) of **11** are obtained as colorless crystals (mp 47–48 °C): ^{1}H NMR δ 2.5–3.7 (m, 8 H), 3.76 (s, 3 H, CO_2Me), 7.5–8.1 (m, 5 H, C_6H_5); IR 1740 (CO_2Me), 1725 (C=O), 1325, 1150 (SO_2). Anal. Calcd for $C_{13}H_{16}O_5S$: C, 54.92; H, 5.67; S, 11.28. Found: C, 55.25; H, 5.92; S, 11.51.

Methyl 7,7-Bis(methoxycarbonyl)-4-oxoheptanoate (12). 3a (1.07 g, 5.00 mmol), dimethyl malonate (1.32 g, 10.0 mmol), and 0.125 mL of Triton B solution are heated to 70 °C for 4 h. The mixture is dissolved in CH_2Cl_2, washed with 2 N HCl, saturated $NaHCO_3$, and brine, dried with $MgSO_4$, concentrated, and distilled (bp 175 °C (0.02 mm)), providing 848 mg (62%) of **12**: ^{1}H NMR δ 1.9–3.0 (m, 8 H), 3.48 (t, J = 7 Hz, 1 H, CH), 3.70 (s, 3 H, CO_2Me), 3.76 (s, 6 H, 2 CO_2Me); IR 1740 (CO_2Me), 1725 (CO). Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.61. Found: C, 52.62; H, 7.14.

Methyl 7-(Methoxycarbonyl)-4,8-dioxononanoate (13). 3a (1.07 g, 5.00 mmol), methyl acetoacetate (1.16 g, 10.0 mmol), and 0.125 mL of Triton B solution are heated to 70 °C for 7 h. Workup as above affords after distillation (bp 145 °C (0.02 mm)) 796 mg (62%) of **13**: ^{1}H NMR δ 2.30 (s, 3 H, COMe), 2.0–2.8 (m, 8 H), 3.56 (t, J = 7 Hz, 1 H, CH), 3.70, 3.76 (2 s, 6 H, 2 CO_2Me); IR 1745 (CO_2Me), 1725 (C=O). Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02. Found: C, 56.20; H, 7.25.

Methyl 7,7-Bis(methylsulfonyl)-4-oxoheptanoate (14). 3a (1.07 g, 5.00 mmol), bis(methylsulfonyl)methane (1.72 g, 10.0 mmol), and 0.125 mL of Triton B solution are dissolved in 20 mL of THF and heated to 70 °C for 4 h. Workup as above gives a colorless crystalline mass, from which 582 mg (37%) of **14** could be isolated as colorless needles (mp 120–123 °C) by fractional crystallization from methanol. The analytical sample is recrystallized from methanol (mp 122 °C): ^{1}H NMR δ 2.4–3.2 (m, 8 H), 3.32 (s, 6 H, 2 SO_2Me), 3.76 (s, 3 H, CO_2Me), 4.36 (t, J = 7 Hz, 1 H, CH); IR (KBr) 1735 (CO_2Me), 1710 (C=O), 1310, 1130 (SO_2). Anal. Calcd for $C_{10}H_{18}O_7S_2$: C, 38.20; H, 5.77; S, 20.39. Found: C, 38.39; H, 5.99; S, 21.07.

General Procedure for Synthesis of Nitroalkane Adducts. Vinylcyclopropane **3a**, **3b**, or **6** and 0.08 equiv of Triton B (40% in methanol) are dissolved in 40–70 equiv of the corresponding nitroalkane and heated for 4 h to 70 °C. After evaporation of the excess of nitroalkane, the residue is taken up in CH_2Cl_2 and washed with 2 N HCl, saturated $NaHCO_3$, and brine. Drying with $MgSO_4$ and Kugelrohr distillation provides the analytically pure nitroalkane adducts **15–19**.

Methyl 7-Nitro-4-oxoheptanoate (15). 3a (1.07 g, 5.00 mmol), nitromethane (20 mL, 264 mmol), and 0.125 mL of Triton B solution yield 760 mg (75%) of **15** as a colorless liquid (bp 145 °C (0.02 mm)): ^{1}H NMR 1.9–2.9 (m, 8 H), 3.57 (s, 3 H, CO_2Me), 4.36 (t, J = 7 Hz, 2 H, CH_2NO_2); IR 1745 (CO_2Me), 1725 (C=O), 1365 (NO_2). Anal. Calcd for $C_8H_{13}NO_5$: C, 47.29; H, 6.49; N, 6.89. Found: C, 47.87; H, 6.87; N, 6.46.

Methyl 7-Nitro-4-oxooctanoate (16). 3a (860 mg, 4.00 mmol), nitroethane (20 mL, 282 mmol), and 0.1 mL of Triton B solution deliver 790 mg (91%) of **16** as a colorless liquid (bp 110 °C (0.02 mm)): ^{1}H NMR δ 1.41 (d, J = 8 Hz, 3 H, Me), 1.8–2.2, 2.45–2.75 (2 m, 2 H, 6 H), 3.53 (s, 3 H, CO_2Me), 4.51 (sextet, J = 8 Hz, 1 H, $CHNO_2$); IR 1740 (CO_2Me), 1725 (C=O), 1360 (NO_2). Anal. Calcd for $C_9H_{15}NO_5$: C, 49.77; H, 6.96; N, 6.45. Found: C, 50.05; H, 7.17; N, 6.17.

Methyl 7-Methyl-7-nitro-4-oxooctanoate (17). 3a (1.07 g, 5.00 mmol), 2-nitropropane (20 mL, 222 mmol), and 0.125 mL of Triton B solution yield 1.08 g of crude product, which is filtered through a pad of Al_2O_3 (cyclohexane/ethyl acetate, 8:2) before distillation (bp 120 °C (0.02 mm)); 756 mg (65%) of **17** as a colorless liquid: ^{1}H NMR δ 1.60 (s, 6 H, 2 Me), 2.0–2.9 (m, 8 H), 3.70 (s, 3 H, CO_2Me); IR 1745 (CO_2Me), 1725 (C=O), 1345 (NO_2). Anal. Calcd for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.41; N, 6.06. Found: C, 52.41; H, 7.56; N, 6.13.

Methyl 2-Methyl-7-nitro-4-oxoheptanoate (18). 3b (1.14 g, 5.00 mmol), nitromethane (20 mL, 264 mmol), and 0.125 mL of Triton B solution afford 726 mg (67%) of **18** as a pale yellow oil: ^{1}H NMR δ 1.28 (d, J = 7 Hz, 3 H, Me), 2.0–3.2 (m, 7 H), 3.70 (s, 3 H, CO_2Me), 4.43 (t, J = 7 Hz, 2 H, CH_2NO_2); IR 1745 (CO_2Me), 1730 (C=O), 1370 (NO_2). Anal. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96; N, 6.45. Found: C, 49.54; H, 7.02; N, 6.57.

Methyl 2-[2-Oxo-4-(nitromethyl)cyclohexyl]acetate (19). **6** (1.20 g, 5.00 mmol), nitromethane (20 mL, 264 mmol), and 0.125 mL of Triton B solution yield 952 mg of pale yellow crude product, which is pure according to NMR spectroscopy. The analytical sample is obtained by distillation (bp 120–160 °C (0.02 mm)) as a semicrystalline mass: mp 40–54 °C; ^{1}H NMR δ 1.1–3.3 (m, 10 H) 3.70 (s, 3 H, CO_2Me), 4.40 (d, J = 7 Hz, CH_2NO_2); ^{13}C NMR trans isomer δ 28.4, 30.9, 33.4 (3t), 37.8 (d), 44.1 (t), 46.0 (d), 51.4 (q), 79.9 (t, CH_2NO_2), 172.3 (s), 206.9 (s); cis isomer δ 25.7, 27.6, 33.5 (3t), 35.6 (d), 43.0 (t), 45.9 (d), 51.9 (q), 77.2 (t, CH_2NO_2), 172.3 (s), 207.6 (s); trans:cis = 87:13; IR 1745 (CO_2Me), 1725 (C=O), 1360 (NO_2). Anal. Calcd for $C_{10}H_{15}NO_5$: C, 52.40; H, 6.60; N, 6.11. Found: C, 52.56; H, 7.20; N, 6.19.

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Registry No. **3a**, 90288-82-7; **3b**, 90288-83-8; *cis*-**6**, 99377-02-3; *trans*-**6**, 99377-15-8; **7**, 53914-28-6; **8**, 99377-03-4; **9**, 99377-04-5; **10**, 99377-05-6; **11**, 99377-06-7; **12**, 99377-07-8; **13**, 99377-08-9; **14**, 99377-09-0; **15**, 99377-10-3; **16**, 99377-11-4; **17**, 99377-12-5; **18**, 99377-13-6; *cis*-**19**, 99377-14-7; *trans*-**19**, 99377-14-7; $Cu(Acac)_2$, 13395-16-9; MeOH, 67-56-1; PhSH, 108-98-5; Et_2NH, 109-89-7; $NaNO_2$, 7632-00-0; $NaSO_2Ph$, 873-55-2; $(MeO_2C)_2CH_2$, 108-59-8; MeO_2CCH_2COMe, 105-45-3; $(MeO_2S)_2CH_2$, 1750-62-5; $MeNO_2$, 75-52-5; $EtNO_2$, 79-24-3; Me_2CHNO_2, 79-46-9; methyl diazoacetate, 6832-16-2; 2-(trimethylsiloxy)buta-1,3-diene, 38053-91-7; 2-(trimethylsiloxy)cyclohexa-1,3-diene, 54781-19-0.

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(10) For use of this and other fluoride sources, see ref 3a.