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MANGANESE (III) BASED OXIDATIVE FREE-RADICAL ANNULATIONS

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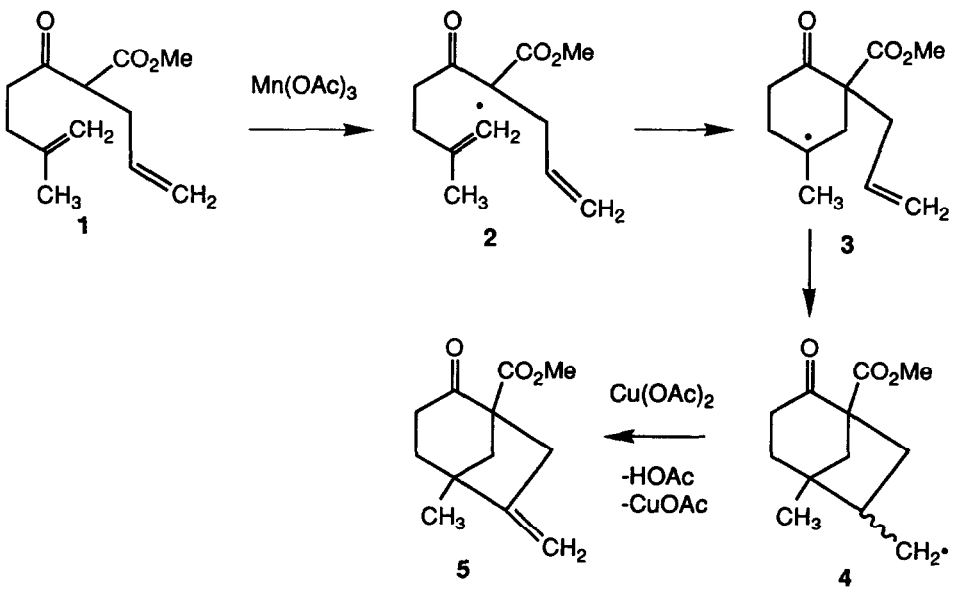
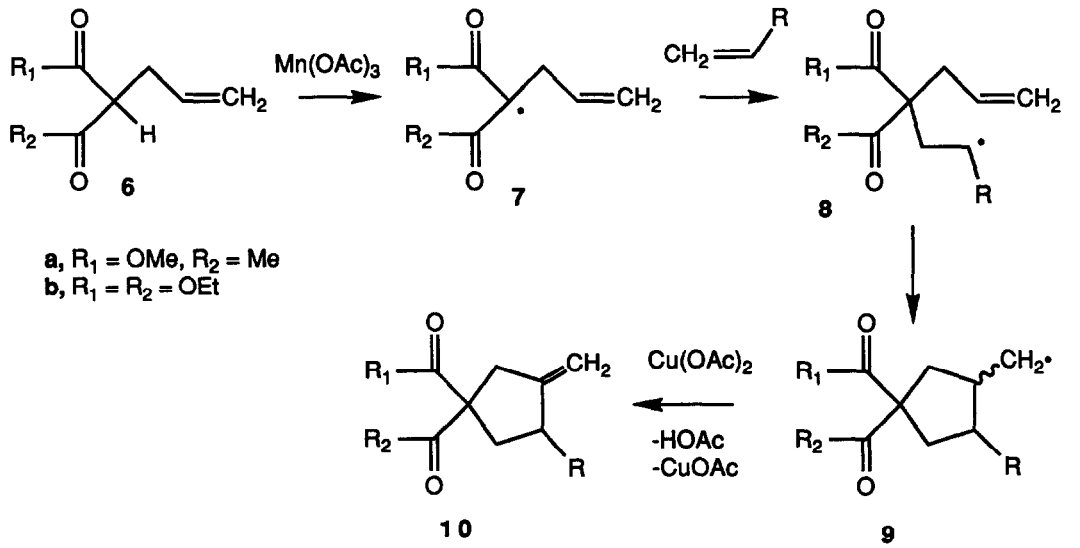
Abstract: Reaction of diethyl allylmalonate (**6b**), sterically accessible nucleophilic alkenes, $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ gives methylenecyclopentanes **13** to **17** in 17-100% yield by an oxidative free-radical annulation. Similarly, oxidative annulation of diethyl crotylmalonate and ethyl benzylacetoacetate with an alkene gives vinylcyclopentane (**30**) and tetralin (**35**).

Introduction

We recently reported[1d] the oxidative cyclization of unsaturated β–ketoesters such as **1** with two equivalents of manganic acetate[1-3] and a catalytic amount of cupric acetate to give the bicyclo[3.2.1]octane **5** in 86% yield. Oxidation of **1** by manganese (III) gives the electrophilic enol radical **2** which adds to the double bond to give the nucleophilic tertiary radical **3**.[4] Radical **3** undergoes the expected 5-*exo*-cyclization to give radical **4** as a mixture of stereoisomers.[4] Radical **4** reacts with cupric acetate[5] to give a copper (III) intermediate which undergoes oxidative β–hydride elimination to give bicyclo[3.2.1]octane **5**. The copper (I) produced in this oxidation is reoxidized to copper (II) by the second equivalent of manganese (III). Oxidative free-radical cyclization of **1** provides an efficient route to highly functionalized bicyclic compounds.



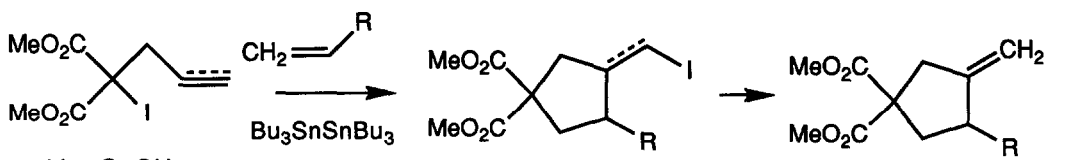
If the first cyclization could be replaced by the intermolecular addition of the enol radical to an alkene, this sequence of reactions would provide an attractive procedure for the preparation of methylenecyclopentanes. The oxidative addition of dialkyl malonates and ethyl acetoacetate to alkenes with manganic acetate has been extensively explored.[3,6] Oxidation of methyl 2-allylacetoacetate (**6a**) or diethyl allylmalonate (**6b**) with manganic acetate will give enol radical **7** which should add to an alkene to give **8**. Cyclization of **8** to give **9** and oxidation by cupric acetate to give **10** will proceed analogously to the conversion of **3** to **5**.



6 **7** **8** **9** **10**

a, R_1 = OMe, R_2 = Me
b, R_1 = R_2 = OEt

Curran and coworkers have prepared methylenecyclopentanes by atom transfer annulations.[4g,7] Reaction of dimethyl iodoallylmalonate (**11a**) or iodopropargylmalonate (**11b**) with simple alkenes in the presence of hexabutylditin gives **12**. Alkyl iodide **12a** can be converted to **10** by dehydrohalogenation. Alkenyl iodide **12b**, and isomeric iodides, can be converted to **10** by reduction with tri-*n*-butyltin hydride. The proposed conversion of **6** to **10** by oxidative annulation with manganic acetate and cupric acetate provides a simpler one-pot method for the conversion of **6** to **10**.[8]



11a, C=CH_2
11b, C≡CH

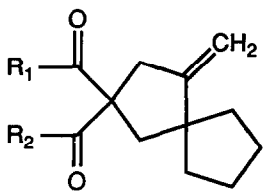
12a, -CH_2I
12b, =CHI

10

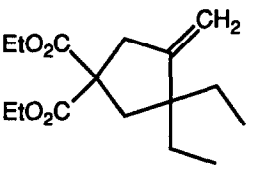
Results and Discussion

Reaction of methyl allylacetoacetate (**6a**) with methylenecyclopentane and $Mn(OAc)_3 \cdot 2H_2O$ (4 equivalents) and $Cu(OAc)_2 \cdot H_2O$ (1 equivalent) in acetic acid for 16 h at 25 °C gives 75% of **13a**. A similar reaction with diethyl allylmalonate (**6b**) for 24 h at 75 °C gives a quantitative yield of **13b**. Higher reaction temperatures are required for the reaction of **6b** because the malonate α–proton is less acidic than the acetoacetate α–proton. Although only 2 equivalents of $Mn(OAc)_3 \cdot 2H_2O$ and a catalytic amount of $Cu(OAc)_2 \cdot H_2O$ are required, better yields are obtained with excess oxidant. Diethyl allylmalonate was used exclusively for all additional studies since the yields were higher and mixtures of stereoisomers would not be obtained with unsymmetrical alkenes.

Reaction of 1,1-disubstituted alkenes with **6b** proceeds in excellent yield. Addition to 2-ethyl-1-butene gives 86% of **14**. Reaction with mono- and trisubstituted alkenes is not as successful. Monosubstituted alkenes 1-hexene, vinyl acetate and allyltrimethylsilane give **15a** (35%), **15b** (40%) and **15c** (89%), respectively. Trisubstituted alkenes 2-methyl-2-butene and 1-ethylcyclopentene give **16** (17%) and **17** (20%), respectively. Methylenecyclopentanes could not be obtained from cyclohexene, (Z)-4-octene, styrene, ethyl vinyl ether, 1,3-cyclohexadiene, 1-methylcycloheptene and 1-acetoxycyclohexene.



13a, R_1 = OMe, R_2 = Me
13b, $R_1 = R_2$ = OEt



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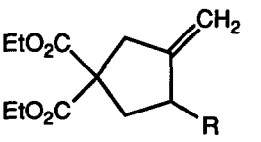
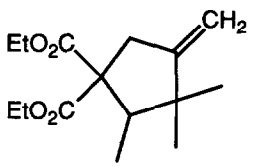


15a, R = *n*-Bu
15b, R = OAc
15c, R = $CH_2Si(Me)_3$



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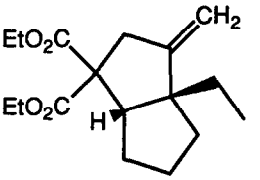

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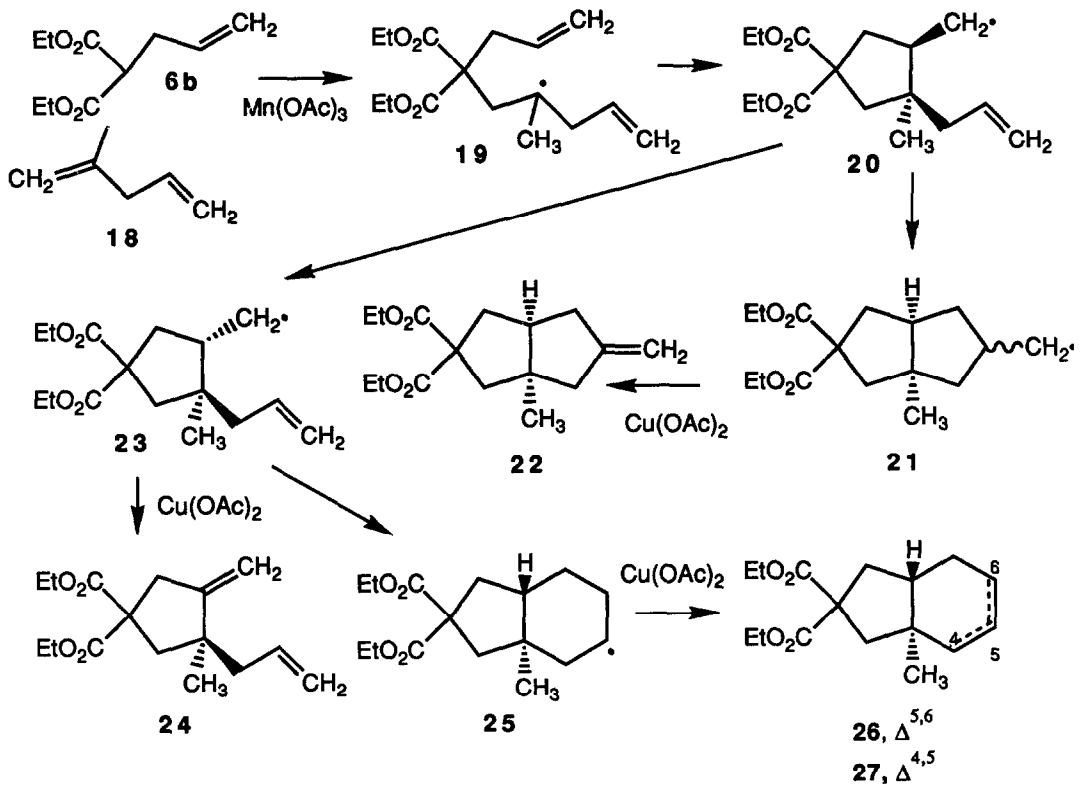
These results indicate the scope and limitation of this oxidative annulation route to **10**. Malonyl radicals have been shown to be electrophilic.[9] As expected, excellent yields are obtained with sterically accessible nucleophilic alkenes such as 1,1-disubstituted alkenes and allyltrimethylsilane. Poorer yields are obtained with sterically accessible but less nucleophilic

terminal alkenes such as 1-hexene. Surprisingly poor yields are obtained with trisubstituted alkenes. Apparently, the addition of radical **7b** to alkenes is very susceptible to steric hindrance.

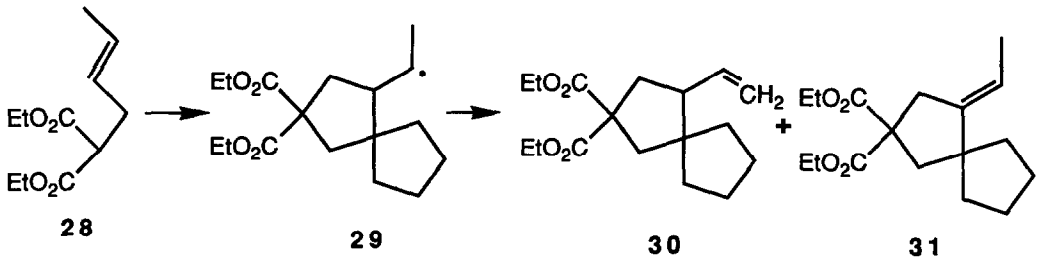
The success of this cycloaddition depends upon the relative rates of the desired and side reactions of radicals **7**, **8**, and **9**. Oxidation of **6b** by manganese (III) gives the electrophilic radical **7b**. Radical **7b** reacts rapidly with sterically accessible nucleophilic alkenes to give **8**. In the absence of a sufficiently reactive alkene, **7b** undergoes oxidative elimination with manganese (III) or copper (II) to give a diene which polymerizes.[1e] Nucleophilic radical **8** is a 5-hexenyl radical and therefore cyclizes rapidly to give the nucleophilic primary radical **9**. Nucleophilic radical **9** reacts slowly with excess alkene but reacts rapidly with copper (II) to give **10**.

Reaction of **6b** with 2-methyl-1,4-pentadiene (**18**) provides a mixture of **22** (12%), **24** (12%), **26** (7%) and **27** (2%). Addition of **7b** to the more nucleophilic double bond of **18** gives **19** which cyclizes to a mixture of **20** and **23**. Radical **20** undergoes the expected fast 5-*exo* cyclization to give **21** which reacts with copper (II) to give **22**. Radical **23** does not undergo a 5-*exo* cyclization since a strained *trans*-fused bicyclo[3.3.0]octane would be formed.[10] A slow 6-*endo* cyclization



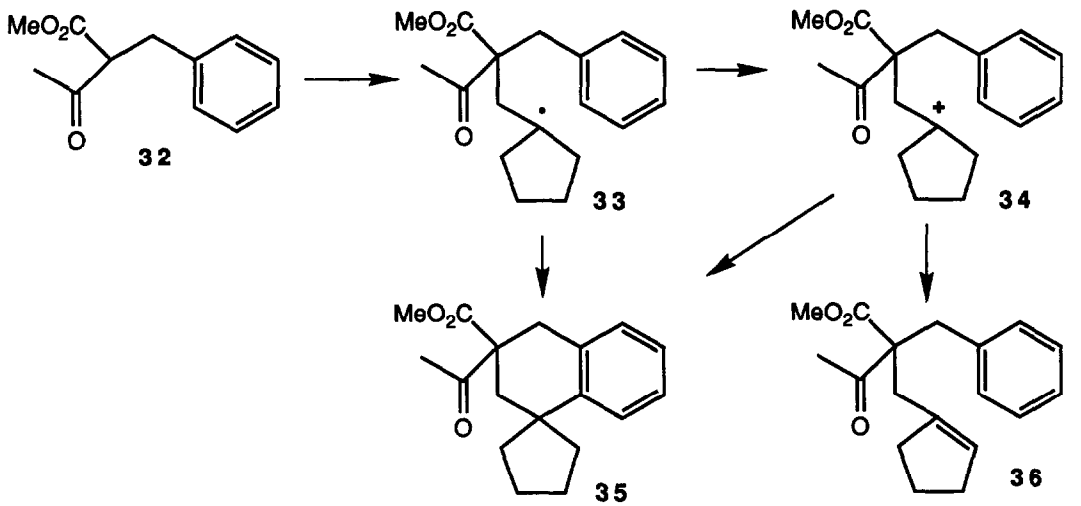
gives **25** which reacts with copper (II) to give **26** and **27**. Because the cyclization to **25** is slow, **23** also reacts with copper (II) to give **24**. Since the cyclization of **23** to **25** is irreversible, the formation of **26** and **27** should be favored at the expense of **24** at low concentrations of copper (II). As expected, reaction of **6b**, **18**, and 4 equivalents of $Mn(OAc)_3 \cdot 2H_2O$ with only 0.05 equivalents of $Cu(OAc)_2 \cdot H_2O$ gives a 6:2:7:2 mixture of **22**, **24**, **26** and **27**. The assignment of the *trans*-ring fusion to **26** and **27** follows from the absorption of the angular methyl group at δ 0.74 and 0.79, respectively.[11]

Oxidative annulation of diethyl crotylmalonate (**28**) to alkenes provides a route to vinylcyclopentanes. Reaction of **28** with methylenecyclopentane gives 49% of an 8:1 mixture of **30** and **31**. Oxidation of **28**, addition of the radical to the alkene, and 5-*exo* cyclization gives **29**. Reaction of **29** with copper (II) can give either the Hofmann product **30** or the Zaitsev product **31**. We have previously shown that the Hofmann product is formed selectively from cyclopentyl ethyl radicals.[1d]



Oxidative addition of an aromatic β-ketoester to an alkene followed by cyclization of the radical on to the aromatic ring offers an attractive route to tetralin derivatives.[12] Reaction of ethyl benzylacetoacetate (**32**) with methylenecyclopentane and 2 equivalents of $Mn(OAc)_3 \cdot 2H_2O$ in acetic acid for 1 h at 25 °C gives 77% of a complex mixture containing **35** and **36** in a 1.4:1 ratio. Oxidation of **32** and addition of the resulting enol radical to methylenecyclopentane gives **33**. Cyclization of the 4-phenylbutyl radical and oxidation by $Mn(OAc)_3 \cdot 2H_2O$ gives the desired tetralin **35**. Oxidation of the tertiary radical by $Mn(OAc)_3 \cdot 2H_2O$ gives tertiary cation **34**. Friedel-Crafts alkylation will give tetralin **35** while loss of a proton will give **36**. Cyclization of radical **33**, rather than oxidation to cation **34**, should be favored at low concentrations of manganese (III). We were delighted to find that slow addition of solid $Mn(OAc)_3 \cdot 2H_2O$ over 9 h to a solution of **32** and methylenecyclopentane in acetic acid at 25 °C gives 79% of tetralin **35**. Under these reaction conditions cyclization of **33** prior to oxidation is the exclusive pathway.

These results demonstrate that oxidative annulation of unsaturated β-ketoesters and malonates with alkenes provides a short route to tetralins, methylene- and vinylcyclopentanes. The operational simplicity makes it the method of choice with nucleophilic unhindered alkenes.



Experimental Section

General. NMR spectra were recorded on a Varian XL 300 NMR spectrometer in $CDCl_3$. Chemical shifts are reported in δ; coupling constants are reported in Hz. Capillary GC was performed on a Perkin–Elmer 8310 Gas Chromatograph (30 m X 0.25 mm SUPEROX on fused silica) using the following operating program: 60 °C to 150 °C at 10 °C/min followed by 5 min at 150 °C, then 150 °C to 190 °C at 20 °C/min followed by 8 min at 190 °C; He flow 25 cc/min. $Mn(OAc)_3 \cdot 2H_2O$ and Diethyl allylmalonate were purchased from Aldrich Chemical Co. Methyl 2-allylacetoacetate[13] and diethyl crotylmalonate[14] were prepared by the literature procedure. All reactions were carried out under nitrogen.

Methyl 2–Acetyl–4–methylenespiro[4.4]nonane–2–carboxylate (13). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6a** (0.156 g, 1 mmol) and methylenecyclopentane (0.082 g, 1 mmol). The solution was stirred for 16 h at room temperature, treated with 5 mL of saturated $NaHSO_3$ solution to reduce unreacted Mn(III), and diluted with 20 mL of water. This solution was extracted with three portions of methylene chloride. The combined organic layers were washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated in vacuo to afford 0.303 g of a yellow oil which was evaporatively distilled (90 °C, 0.01 Torr) to afford 0.177 g (75%) of **13**: ^1H NMR 4.85 (dd, 1, J = 1.9, 1.9), 4.77 (dd, 1, J = 1.9, 1.9), 3.74 (s, 3), 3.05 (ddd, 1, J = 16.5, 1.9, 1.9), 2.97 (ddd, 1, J = 16.5, 1.9, 1.9), 2.31 (d, 1, J = 13.6), 2.21 (d, 1, J = 13.6), 2.16 (s, 3), 1.80–1.50 (m, 8); ^{13}C NMR 203.4, 173.3, 156.6, 104.2, 64.3, 53.1, 52.6, 45.7 (2 C), 40.1, 39.8, 39.7, 26.2, 24.5; IR (neat) 2920, 2830, 1740, 1710, 1660, 1430, 1350, 875 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.04; H, 8.89.

Diethyl 4–Methylenespiro[4.4]nonane–2,2–dicarboxylate (14a). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and methylenecyclopentane (0.082 g, 1 mmol). The resultant dark brown solution was heated at 70–75 °C for 24 h and worked–up as above to

afford 0.348 g of a yellow oil which was evaporatively distilled (90 °C, 0.05 Torr) to give 0.280 g (100%) of **14a**: ^{1}H NMR 4.86 (dd, 1, J = 2, 2), 4.78 (dd, 1, J = 2, 2), 4.19 (q, 4, J = 7.2), 3.04 (t, 2, J = 2), 2.33 (s, 2), 1.71–1.57 (m, 8), 1.25 (t, 6, J = 7.2); ^{13}C NMR 172.1 (2 C), 157.0, 104.2, 61.4 (2 C), 57.8, 53.0, 47.0, 41,2, 40.3 (2 C), 24.5 (2 C), 14.0 (2 C); IR (neat) 2800, 1735, 1660, 1450, 1370, 1255, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.04; H, 8.63. Found: C, 68.31; H, 8.70.

Diethyl 3,3–Diethyl–4–methylenecyclopentane–1,1–dicarboxylate (14b). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and 2–ethyl–1–butene (0.084 g, 1 mmol). The resultant dark brown solution was heated at 70–75 °C for 24 h and worked-up as above to give 0.303 g of a yellow oil which was evaporatively distilled (90 °C, 0.01 Torr) to afford 0.243 g (86%) of **14b** as a clear liquid: ^{1}H NMR 4.95 (dd, 1, J = 2, 2), 4.66 (dd, 1, J = 2, 2), 4.18 (q, 4, J = 7.0), 3.00 (t , 2, J = 2.0), 2.29 (s, 2), 1.43 (qd, 2, J = 7.5, 14), 1.33 (qd, 2, J = 7.5, 14) , 1.24 (t, 6, J = 7.0), 0.80 (t, 6, J = 7.5); ^{13}C NMR 172.4 (2 C), 154.7, 106.0, 61.4 (2 C), 57.3, 48.5, 43.3, 41.8, 29.9 (2 C), 14.0 (2 C), 8.6 (2 C); IR (neat) 2800, 1740, 1665, 1470, 1370, 1255, 1185, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.72; H, 9.21.

Diethyl 3–Butyl–4–methylenecyclopentane–1,1–dicarboxylate (15a). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and 1–hexene (0.252 g, 3 mmol). The resultant dark brown solution was heated at 70–75 °C for 14 h and worked-up as above to afford 0.211 g of a yellow oil which was evaporatively distilled (100 °C / 0.1 Torr) to give 0.100 g (35%) of **15a** as a clear liquid of approximately 90% purity. Flash chromatography on silica gel (10:1 Hexanes–EtOAc) afforded an analytical sample: ^{1}H NMR 4.92 (ddd, 1, J = 2, 2, 2), 4.81 (ddd, 1, J = 2, 2, 2), 4.19 (q, 2, J = 7.2), 4.18 (q, 2, J = 7.2), 3.04 (br d, 1, J = 16.7), 2.89 (dddd, 1, J = 16.7, 2, 2, 1.2), 2.58 (ddd, 1, J = 12.2, 7.7, 1.2), 2.54–2.41 (m, 1), 1.77 (dd, 1, J = 12.2, 9.8), 1.7–1.58 (m, 1), 1.40–1.20 (m, 5), 1.25 (t, 6, J = 7.2), 0.90 (br t, 3, J = 7); ^{13}C NMR 171.9 (2 C), 152.4, 105.8, 61.4 (2 C), 58.4, 42.3, 40.8, 39.8, 33.7, 29.7, 22.8, 14.0 (2 C), 8.5; IR (neat) 2925, 2910, 1730, 1660, 1460, 1360, 1250, 1180, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.87; H, 9.35.

Diethyl 3–Acetoxy–4–methylenecyclopentane–1,1–dicarboxylate (15b). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and vinyl acetate (0.258 g, 3 mmol). The resultant dark brown solution was heated at 70 °C for 48 h and worked-up as above to afford 0.371 g of a yellow oil which was evaporatively distilled (90 °C, 0.01 Torr) to give 0.113 g (40%) of **15b** as a clear liquid of approximately 90% purity. Flash chromatography on silica gel (10:1 hexanes–EtOAc) afforded an analytical sample: ^{1}H NMR 5.52 (ddddd, 1, J = 2, 2, 2, 4.9, 6.8), 5.21 (ddd, 1, J = 2, 2, 2), 5.16 (ddd, 1, J = 2, 2, 2), 4.25–4.15 (m, 4), 3.21 (br d, 1, J = 16.9), 2.83 (ddd, 1, J = 2, 2, 17), 2.75 (dd, 1, J = 6.8, 14), 2.34 (dd, 1, J = 4.9, 14), 2.03 (s, 3), 1.27 (t, 3, J = 7.1), 1.25 (t, 3, J = 7.1); ^{13}C NMR 171.2, 170.8, 170.4, 146.2, 112.2, 74.9, 61.8, 61.1, 57.7, 39.7, 38.3, 21.1, 14.0, 13.9; IR (neat) 2980, 1735, 1445, 1365, 1230, 1075, 860 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.05; H, 7.03.

Diethyl 3–(Trimethylsilyl)methyl–4–methylenecyclopentane–1,1–dicarboxylate (15c). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and allyltrimethylsilane (0.340 g, 3 mmol). The resultant dark brown solution was heated at 70 °C for 24 h and worked-up as above to afford the product as a yellow oil. Flash chromatography on silica gel (hexanes) afforded **15c** (0.277 g, 89%): ^{1}H NMR 4.89 (ddd, 1, J = 2.1, 2.1, 2.1), 4.83 (ddd, 1, J = 2.1, 2.1, 2.1), 4.28–4.12 (m, 4), 3.07 (br d, 1, J = 17), 2.91 (ddd, 1, J = 2.1, 2.1, 17), 2.60 (dd, 1, J = 3.7, 11.2), 2.55–2.44 (m, 1), 1.77 (dd, 1, J = 11.2, 12.2), 1.25 (t, 3, J = 7.1), 1.24 (t, 3, J = 7.1), 1.01 (dd, 1, J = 3.6, 14.5), 0.50

(dd, 1, J = 10.6, 14.5), 0.15 (s, 9); ^{13}C NMR 172.0, 171.9, 154.8, 105.1, 61.4 (2 C), 58.1, 42.0, 39.9, 39.1, 20.6, 14.0 (2 C), –0.09 (3 C); IR (neat) 2920, 1730, 1705, 1360, 1240, 1160, 830 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_4$: C, 61.50; H, 9.03. Found: C, 61.70; H, 8.93.

Diethyl 2,3,3–Trimethyl–4–methylenecyclopentane–1,1–dicarboxylate (16). To a resealable tube charged with $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 10 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and 2–methyl–2–butene (0.210 g, 3 mmol). The resultant dark brown solution was heated at 70–75 °C for 20 h, and worked–up as above to give 0.327 g of a yellow oil which was purified by evaporative distillation (90 °C, 0.01 Torr) followed by flash chromatography through silica gel (20:1 Hexanes–EtOAc) to afford 0.046 g (17%) of **16**: ^{1}H NMR 4.86 (dd, 1, J = 2, 2), 4.81 (dd, 1, J = 2, 2), 4.25–4.12 (m, 4), 3.37 (ddd, 1, J = 2, 2, 17), 2.67 (ddd, 1, J = 2, 2, 17), 2.57 (q, 1, J = 7.3), 1.26 (t, 3, J = 7.1), 1.25 (t, 3, J = 7.1), 1.09 (s, 3), 1.03 (d, 3, J = 7.3), 0.89 (s, 3); ^{13}C NMR 172.2, 171.5, 158.2, 104.2, 61.2, 61.0, 49.6, 44.0, 40.4, 40.5, 28.2, 23.7, 14.0 (2 C), 11.0; IR (neat) 2940, 1730, 1610, 1460, 1360, 1240, 1180, 1040, 880 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.02. Found: C, 67.15; H, 9.03.

Diethyl *cis*–3a–Ethyl–tetrahydro–3–methylenepentalene–1,1–dicarboxylate (17). To a stirred solution of $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and 1–ethylcyclopentene (0.096 g, 1 mmol). The resultant dark brown solution was heated at 70–75 °C for 36 h, and worked–up as above to give 0.326 g of a yellow oil which was evaporatively distilled (90 °C, 0.01 Torr) to afford 0.113 g of the product contaminated with starting material. Flash chromatography through silica gel (20:1 Hexanes–EtOAc) afforded 0.060 g (20%) of **17**: ^{1}H NMR 4.86 (br s, 1), 4.71 (br s, 1), 4.4–4.2 (m, 4), 3.24 (ddd, 1, J = 2.5, 2.5, 16.4), 3.11 (br dd, 1, 8.1, 8.5), 2.83 (dddd, 1, J = 1.3, 1.3, 1.3, 16.4) 1.9–1.3 (m, 8), 1.25 (t, 3, J = 7.1), 1.23 (t, 3, J = 7.1), 0.92 (t, 3, J = 7.4); ^{13}C NMR 171.8, 170.6, 157.5, 105.0, 61.6, 61.3, 61.2, 57.6, 51.8, 40.5, 39.9, 31.6, 30.9, 26.6, 14.1, 14.0, 9.9; IR (neat) 2930, 2835, 1730, 1650, 1460, 1360, 1260, 1230, 1150, 1100 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.34; H, 9.01.

Diethyl *cis*–octahydro–3a–methyl–5–methylenepentalene–2,2–dicarboxylate (22), Diethyl 3–Methyl–4–methylene–3–(2–propenyl)cyclopentane–1,1–dicarboxylate (24), Diethyl *trans*–2,3,3a,4,7,7a–Hexahydro–3a–methyl–[1H]–indene–2,2–dicarboxylate (26) and Diethyl *trans*–2,3,3a,6,7,7a–Hexahydro–3a–methyl–[1H]–indene–2,2–dicarboxylate (27). To a resealable tube charged with $Mn(OAc)_3 \cdot 2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **6b** (0.200 g, 1 mmol) and **18** (0.246 g, 3 mmol). The solution was heated to 90 °C for 48 h at which time it was worked–up as above. Flash chromatography on silica gel (15:1 hexanes–EtoAc) afforded a clear liquid (0.101 g, 40%) consisting of **6b, 24, 22, 26,** and **27** in a 0.9:1:1:0.55:0.15 ratio determined by capillary GC (t_R=5.0, 9.3, 10.4, 12.0 and 12.0 min, respectively) which was separated by preparative GC (3/8" X 7' 10% XF–1150 on PAW 60/80, 170 °C, He flow 34 cc/min, t_R=10.2, 33.6, 43.8, 67.8, 67.8 min, respectively):

The data for **24**: ^{1}H NMR 5.76 (tdd, 1, J = 7.3, 10.4, 16.7), 5.05 (br d, 1, J = 10.4), 5.04 (br d, 1, J = 16.7), 4.93 (dd, 1, J = 2.0, 2.0), 4.76 (dd, 1, J = 2.0, 2.0), 4.17 (q, 4, J = 7.1), 3.05 (ddd, 1, J = 2, 2, 16.7), 3.02 (ddd, 1, J = 2, 2, 16.7), 2.40 (d, 1, J = 13.9), 2.20 (d, 1, J = 13.9), 2.1 (br d, 2, J = 7.3), 1.25 (t, 6, J = 7.1), 1.07 (s, 3); ^{13}C NMR 172.1 (2 C), 156.6, 135.0, 117.6, 105.5, 61.5 (2 C), 57.7, 46.0, 45.1, 44.7, 41.2, 26.8, 14.0 (2 C); IR 3095, 2990, 2920, 1760, 1260, 1190, 1080, 990, 910, 880 cm^{-1}.

The data for **22**: ^{1}H NMR 4.82 (br s, 2), 4.18 (m, 4), 2.55 (br dd, 1, J = 13.3, 8.0, 0.8), 2.6–2.4 (m, 1), 2.4–2.1 (m, 5), 1.85 (dd, 1, J = 13.3, 9.0), 1.25 (t, 3, J = 7.1), 1.23 (t, 3, J = 7.1), 1.06 (s, 3); ^{13}C NMR 151.5, 107.0, 61.4 (2 C), 57.3, 50.1, 47.3, 46.6, 43.4, 40.6, 37.6, 27.3, 14.0 (2 C) (missing 2 carbonyl carbons); IR 2995, 2950, 1745, 1460, 1242, 1195, 886 cm^{-1}.

The spectral data for **26** and **27** were determined from the 4.4:1 mixture: ^{1}H NMR (**26**) 5.64 (br d, 1, J = 9), 5.60 (br d, 1, J = 9), 4.20 (m, 4), 2.42 (d, 1, J = 13.4), 2.38 (dd, 1, J = 13.2, 5.4), 2.03 (br s, 2), 2.2–2.0 (m, 1), 1.94 (dd, 1, J = 13.2, 4.1), 2.0–1.6 (m, 3), 1.25 (t, 3, J = 7.1), 1.23 (t, 3, J = 7.1), 0.74 (s, 3); (**27**) 5.88 (dt, 1, J = 9.7, 2.5), 5.44 (dt, 1, J = 9.7, 3.6), 0.79 (s, 3); ^{13}C NMR (**26**) 126.5, 126.4, 61.8, 61.7, 57.8, 48.1, 43.1, 40.4, 39.8, 37.7, 27.3, 17.6, 14.1, 14.0 (missing 2 carbonyl carbons); IR 3030, 2980, 2870, 1747, 1470, 1247, 1210, 1190, 1070 cm^{-1}.

Diethyl 4–Ethenylspiro[4.4]nonane–2,2–dicarboxylate (30) and Diethyl 4–(*E*)–Ethylidenespiro[4.4]nonane–2,2–dicarboxylate (31). To a stirred solution of $Mn(OAc)_3$•$2H_2O$ (1.07 g, 4 mmol) and $Cu(OAc)_2$•H_2O (0.200 g, 1 mmol) in 40 mL of glacial acetic acid was added **28** (0.214 g, 1 mmol) and methylenecyclopentane (0.082 g, 1 mmol) and heated to 70 °C for 38 h at which time it was worked–up as above. Flash chromatography on silica gel (20:1 Pet. ether–EtOAc) afforded 0.145 g (49%) of a mixture of **30** and **31** in an 8:1 ratio determined from an average of ^{1}H NMR and capillary GC data (t_R=14.8 and 15.1 min, respectively). The spectral data was determined from the mixture: ^{1}H NMR (**30**) 5.74 (ddd, 1, J = 7.6, 10.7, 16.7), 5.05 (ddd, 1, J = 0.7, 2.1, 10.7), 5.04 (dd, 1, J = 1, 2.1, 16.7), 4.2 (m, 4), 2.45 (ddddd, 1, J = 0.7, 1, 6.6, 7.6, 13.4), 2.44 (dd, 1, J = 6.6, 15.4), 2.40 (d, 1, J = 13.8), 2.10 (d, 1, J = 13.8), 2.14 (dd, 1, J = 13.4, 15.4), 1.8–1.5 (m, 8), 1.25 (t, 3, J = 7.1), 1.24 (t, 3, J = 7.1); (**31**) 5.22 (tq, 1, J = 2.5, 7.0), 4.2 (m, 4), 2.98 (qd, 2, J = 1.5, 2.5), 2.31 (s, 2), 1.8–1.5 (m, 8), 1.62 (td, 3, J = 1.5, 7.0), 1.25 (t, 6, J = 7.1); ^{13}C NMR (**30**) 173.0, 172.7, 137.7, 116.1, 61.4, 61.3, 57.9, 53.7, 51.8, 47.2, 39.1, 37.2, 32.1, 24.7, 24.3, 14.0 (2 C); (**31**) 172.3 (2 C), 157.3, 113.8, 61.3 (2 C), 58.1, 53.2, 47.0, 40.2 (2 C), 24.5 (2 C) 14.4, 14.0 (2 C), (missing one carbon); IR (neat) 2940, 1725, 1635, 1440, 1360, 1250, 1170, 910, 855 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.53; H, 9.02.

Ethyl 3'–Acetyl–3',4'–dihydrospiro[cyclopentane–1,1'(2'H)–naphthalene]–3'–carboxylate (35). $Mn(OAc)_3$•$2H_2O$ (0.54 g, 2 mmol) was added in small portions over 9 h at room temperature to a stirred solution of **32** (0.220 g, 1 mmol) and methylenecyclopentane (0.082 g, 1 mmol) in 20 mL of glacial acetic acid. Upon addition, the reaction mixture would turn yellow–brown then lighten to a pale yellow–pink at which time more $Mn(OAc)_3$•$2H_2O$ was added. The resultant mixture was worked–up as above to afford a clear oil contaminated with 13% of the starting acetoacetate ester, as determined by capillary GC. Flash chromatography on silica gel (10:1 Hexanes–EtOAc) afforded **35** (0.237 g, 79%): ^{1}H NMR 7.26–7.11 (m, 4), 4.20–4.09 (m, 2), 3.38 (d, 1, J = 16), 2.97 (d, 1, J = 16), 2.49 (dd, 1, J = 1, 14), 2.17 (s, 3), 2.05 (d, 1, J = 14), 1.95–1.70 (m, 8), 1.21 (t, 3, J = 7.1); ^{13}C NMR 204.3, 172.6, 144.2, 133.8, 128.5 (CH), 126.6 (CH), 126.8 (CH), 125.4 (CH), 61.4, 59.6, 45.7, 42.4, 41.4, 40.1, 34.4, 25.9, 24.9, 24.8, 13.9; IR (neat) 2920, 1740, 1710, 1480, 1440, 1350, 1205, 750 cm^{-1}. Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.84; H, 8.04.

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