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Synthesis of Highly Functionalized Tropolones By Rhodium(II)-Catalyzed Reactions of Vinyldiazomethanes With Oxygenated Dienes

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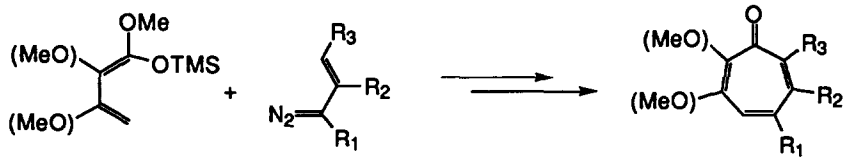
Abstract: Rhodium(II) catalyzed decomposition of vinyldiazomethanes to vinylcarbenoids in the presence of oxygenated dienes leads to the regioselective synthesis of cycloheptadienes by a tandem cyclopropanation/Cope rearrangement. The resulting cycloheptadienes are readily hydrolyzed and oxidized, leading to a very direct and general synthesis of highly functionalized tropolones.

The synthesis of highly functionalized tropolones has drawn considerable interest because the tropolone ring is present in a number of natural products.[1,2] The most general synthetic approaches have been through expansion of six-membered rings[3-8] or by cycloadditions.[9-15] This paper describes a systematic study to develop an alternative general entry to highly functionalized tropolones though the reaction between vinylcarbenoids[16] and dienes as illustrated in Scheme 1. The focus of this work was directed towards the predictable synthesis of highly oxygenated tropones.

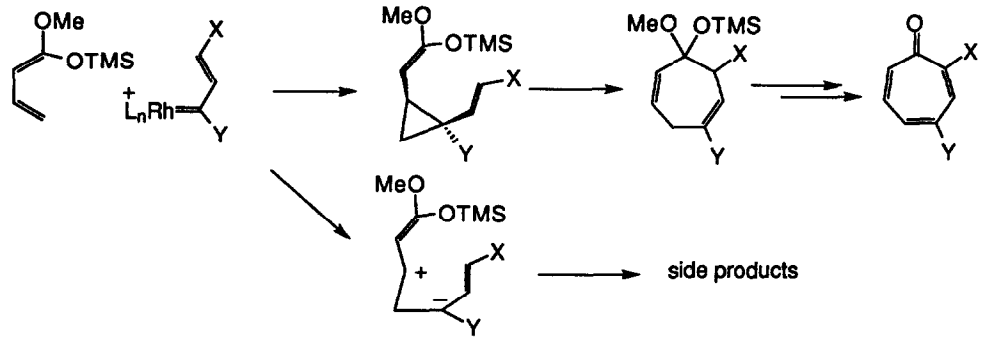
Scheme 1



We have previously described the application of rhodium(II) stabilized vinylcarbenoids for the general synthesis of tropones as illustrated in Scheme 2.[17] The reaction proceeds by a tandem cyclopropanation/Cope rearrangement. A crucial feature of this chemistry is that vinylcarbenoid cyclopropanations proceed with very high stereoselectivity favoring formation of cis divinylcyclopropanes, which then readily rearrange to cycloheptadienes. Most of the vinyldiazomethanes that were used in the earlier study contained two electron withdrawing groups. Major side reactions through the intermediacy of zwitterionic species were avoided by use of non-polar solvents. Expansion of this work to the synthesis of tropolones and other oxygenated tropones would require the use of very electron rich dienes. Thus a major emphasis of the current study into the synthesis of tropolones was to evaluate what dienes may be successfully used for seven-membered ring formation in the

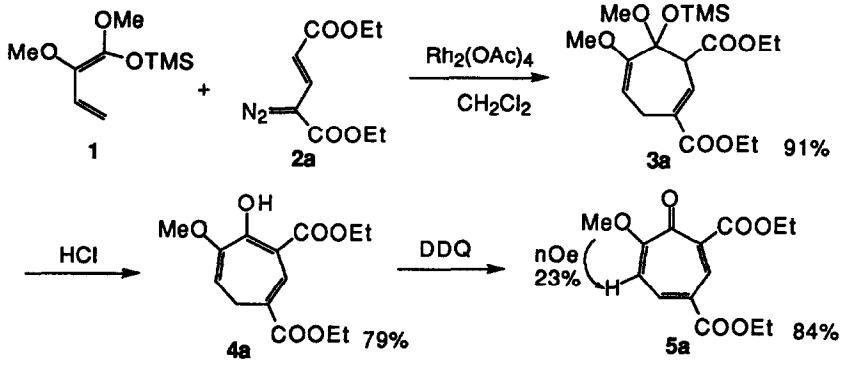
reaction of vinylcarbenoids. A second feature of this work was the use of new types of vinylcarbenoids with particular emphasis on whether electron donating groups can be successfully incorporated into the vinylcarbenoid.

Scheme 2



The first diene that was examined was 1,2-dimethoxy-1-(trimethylsiloxy)butadiene (1) as this diene could lead to the synthesis of methyl tropolones in a regiospecific manner. Normally, methylation of tropolones produces a mixture of two methylated products[1,2] and so, the direct synthesis of methylated tropolones in a predictable manner was considered to have significant practical advantages. Rhodium(II) acetate catalyzed decomposition of the vinyldiazomethane **2a** proceeded very cleanly to form the cycloheptadiene **3a** in 91% yield. Hydrolysis of the silyl ketal protecting group in **3a** was readily achieved by treatment with dilute HCl to generate the cycloheptatrienol **4a** in 79% yield. DDQ oxidation of **4a** proceeded smoothly to give the tropolone **5a** in 84% yield. Confirmation that the hydrolysis of **3a** had proceeded uneventfully was obtained from the nOe analysis of **5a** which clearly showed that the methoxy group was still positioned adjacent to a vinylic hydrogen.

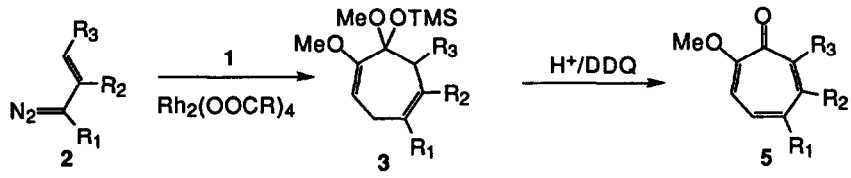
Scheme 3



The reaction could be extended to a range of vinyldiazomethanes and the results are summarized in Table 1. In most instances, the catalyst/solvent system of rhodium(II) pivalate/hexane was used as this combination

limits any possibility of side-reactions occurring through dipolar intermediates.[17,18] In addition to HCl followed by DDQ, two other hydrolysis/oxidation conditions were employed to convert the cycloheptadiene to the tropolone. Citric acid followed by DDQ was preferred for labile systems such as **5d** and **5g**, while a combination of TosOH/DDQ resulted in the direct conversion of **3** to **5**. Unlike the case for **3a**, the cycloheptadienes **3c** and **3g** were unstable and were used in subsequent reactions without chromatographic purification, leading to the formation of the tropones **5c** and **5g** in 46 and 67% yields, respectively.

Table 1: Synthesis of tropolones **5**.

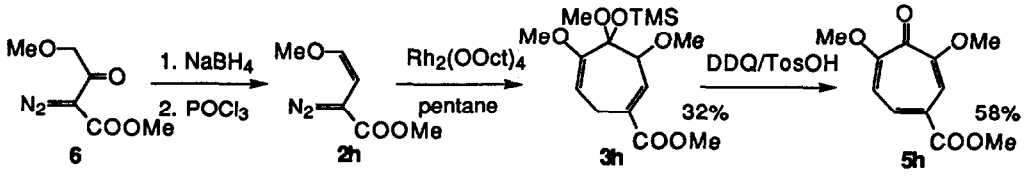


Substrate	R1	R2	R3	product	yield, %	product	yield, %
2a	COOEt	H	COOEt	**3a**	91	**5a**	67[b]
2b	COO^{t}Bu	H	Ph	**3b**	91	**5b**	91[b]
2c	COOEt	H	SPh	**3c**	-[a]	**5c**	46[c]
2d	COOMe	cyclo-$(CH_2)_3$-		**3d**	68	**5b**	80[b]
2e	COOEt	cyclo-$(CH_2)_4$-		**3e**	62	**5e**	59[b]
2f	COO^{t}Bu	H	H	**3f**	60	**5f**	60[b]
2g	COOMe	H	Me	**3g**	-[a]	**5g**	67[c]

a: compound was unstable to chromatography; b: overall yield from **3**; c: overall yield from **2**.

A further notable example is the reaction with the methoxy substituted vinyldiazomethane **2h** as this leads to introduction of an additional methoxy group in the final tropone **5h**. As **2h** contains an electron donating group the chemistry is more challenging because the vinyldiazomethane has limited stability. However, reaction of freshly prepared **2h** gave the cycloheptadiene **3h** in 32% yield (based on the vinyldiazomethane precursor **6**[19]). A one pot oxidation/hydrolysis of **3h** using TosOH/DDQ gave the tropolone **5h** in 58% yield.

Scheme 4



Attempts were then made to extend the chemistry by using 1,3-dimethoxy-1-(trimethylsiloxy)butadiene (7) as the diene. Neither rhodium(II) acetate or rhodium(II) pivalate catalyzed decomposition of **2a** in the presence of **7** generated cycloheptadiene products. Application of the reaction, however, to vinyldiazomethanes that contained less electron withdrawing groups than **2a** did enable formation of cycloheptadiene products in certain cases. Rhodium(II) pivalate catalyzed decomposition of **2i** in the presence of **7** with hexane as solvent gave the cycloheptadiene **8i**. As **8i** was unstable to chromatography, it was directly converted to **9i** without purification by treatment with $VO(OEt)Cl_2$. This resulted in the formation of **9i** in 64% overall yield from **2i**. Confirmation that hydrolysis of **8i** had proceeded uneventfully was obtained through nOe analysis of **9i** which showed enhancement to the two adjacent vinylic protons on irradiation of the methoxy group. The reaction sequence could be extended to other substrates and the results are summarized in Table 2.

Scheme 5

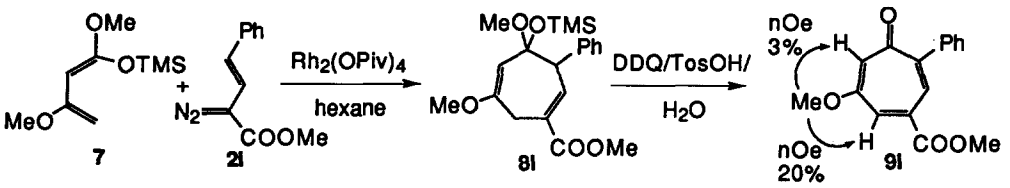
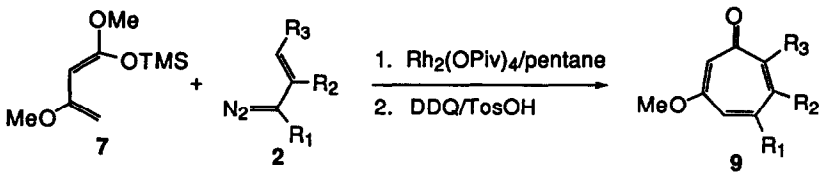


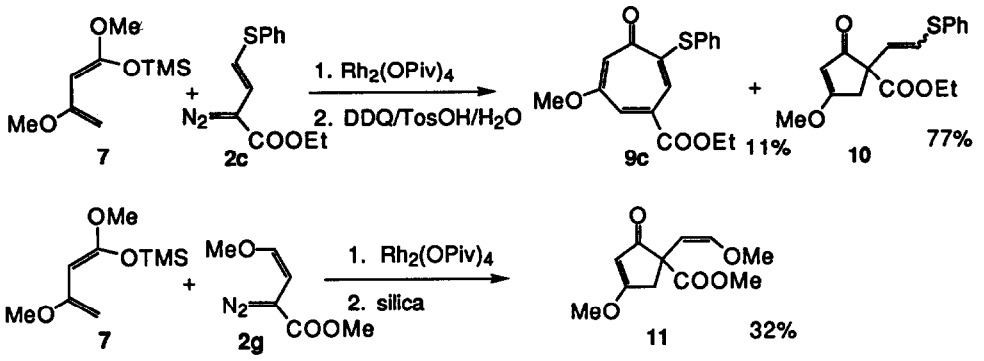
Table 2. Synthesis of 3-methoxytropones



substrate	R1	R2	R3	product	yield, %
2c	COOEt	H	SPh	**9c**	11
2g	COOMe	H	Me	**9g**	58
2i	COOMe	H	Ph	**9i**	64
2j	COOMe	H	SEt	**9j**	39

Further demonstration of the effect of the 3-methoxy substituent was seen in the reaction of **7** with the thiophenyl vinyldiazomethane **2c**. Even though **2c** had reacted cleanly with the 2-methoxy substituted diene **1**, the same reaction sequence with the 3-methoxy substituted diene **7** followed by oxidation/hydrolysis gave a mixture of two products. The tropone **9c** was formed as a minor product, while the major product was the cyclopentenone **10** presumably formed via zwitterionic intermediates. A similar problem was seen in the methoxy substituted vinyldiazomethane **2h** where the only isolated product from the reaction of **2h** with **7** was the cyclopentenone **11**.

Scheme 6



In summary, the reactions between vinyldiazomethanes and oxygenated dienes leads to the synthesis of a variety of tropolones. The reactions are extremely efficient with the 2-methoxy substituted diene **1**, but side products are prevalent in many reactions with the 3-methoxy substituted diene **7**. Presumably, a 3-methoxy substituent on the diene would stabilize zwitterionic intermediates which would enhance the formation of side-product instead of the direct cyclopropanation.

EXPERIMENTAL SECTION

General Section. Dichloromethane was distilled over calcium hydride. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded on a Varian VXR-200 spectrometer. IR spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Low resolution mass spectral determinations were carried out on a Hewlett Packard 5890 Series II GC interfaced with a Hewlett Packard 5989A mass selective detector operating at 70 eV. 1,2-Dimethoxy-1-(trimethylsiloxy)butadiene (**1**),[20] 1,3-dimethoxy-1-(trimethylsiloxy)butadiene (**7**)[20] and the vinyldiazomethanes **2**[18,19] were prepared by literature procedures or variations thereof.

Rhodium(II) Carboxylate Catalyzed Decomposition of Vinyldiazomethanes 2 in the Presence of 1. General Procedure. A solution of **2** (5 mmol) in CH_2Cl_2 or hexane (10 mL) was added over 10 min to a stirred mixture of rhodium(II) carboxylate (0.05 mmol) and **1** (10 mmol) in CH_2Cl_2 (10 mL), heated under reflux in an argon atmosphere. After heating for a further 10 min, the solvent was evaporated under reduced pressure and the excess diene was removed by short path distillation (40-50 °C, 0.5 mm Hg). All products were purified by column chromatography. The quantity of **2**, the catalyst, reaction solvent, and purification absorbent and eluent used are listed in abbreviated form in that order.

Diethyl 4,5-Dimethoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1,3-dicarboxylate (3a). **2a** (1.06 g, 5 mmol), rhodium(II) acetate, CH_2Cl_2, silica, diethyl ether/ petroleum ether (1:4); yield 1.75 g (91%) of a white solid: m.p. 55-58 °C; IR (neat) 2985, 2980, 2900, 2800, 1730, 1700, 1645, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (dd, 1 H, J = 6.6, 2.4 Hz), 4.80 (dd, 1 H, J = 9.5, 3.4 Hz), 4.15 (2q, 4 H, J = 7.3 Hz), 3.85 (dd, 1 H, J = 6.6, 2.0 Hz), 3.47 (s, 3 H), 3.26 (s, 3 H), 3.25 (dd, 1 H, J = 18.2, 9.5 Hz) 2.97 (br d, 1 H, J = 18.2 Hz), 1.27 (t, 6 H, J = 7.3 Hz), 0.71 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 168.9, 166.6, 154.5, 136.1, 134.7, 96.9, 97.5, 60.7, 60.7, 53.6, 52.8, 51.0, 22.9, 14.0, 13.9, 1.5. Anal. Calcd for $C_{18}H_{30}O_7Si$: C, 55.93; H, 7.82. Found: C, 55.93; H, 7.83.

Dimethylethyl 4,5-Dimethoxy-3-phenyl-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (3b). 2b (1.22 g, 5.00 mmol), rhodium(II) acetate, CH_2Cl_2, silica, diethyl ether/ petroleum ether (1:4); yield 1.68 g (91%) of a colorless oil: IR (neat) 3060, 3020, 2985, 2900, 2830, 1700 br, 1600, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34-7.21 (m, 5 H), 6.83 (dd, 1 H, J = 6.6, 2.3 Hz), 4.85 (dd, 1 H, J = 8.6, 4.6 Hz), 3.90 (dd, 1 H, J = 6.6, 2.3 Hz), 3.29 (s, 3 H), 3.26-3.16 (m, 2 H), 3.23 (s, 3 H), 1.45 (s, 9 H), -0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 167.1, 154.8, 139.1, 138.1, 132.3, 130.6, 127.6, 127.0, 101.0, 95.6, 80.3, 53.7, 53.1, 50.0, 28.1, 1.7. The product was of insufficient stability to obtain elemental analysis.

Methyl 1,2,3,5,8,8a-Hexahydro-7,8-dimethoxy-8-[(trimethylsilyl)oxy]azulene-4-carboxylate(3d). 2d (0.830 g, 5 mmol), rhodium(II) pivalate, hexane, alumina, diethyl ether/ petroleum ether (1:9); yield 1.15 g (68%) of a colorless oil: IR (neat) 2920, 2890, 2820, 1690, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.01 (dd, 1 H, J = 10.1, 3.2 Hz), 3.71 (s, 3 H), 3.44 (s, 3 H), 3.30 (dd, 1 H, J = 16.9, 10.0 Hz), 3.15 (s, 3 H), 3.44-1.15 (m, 8 H), 0.50 (s, 9 H). The product was of insufficient stability to obtain elemental analysis.

Ethyl 2,3,4,6,9,9a-Hexahydro-8,9-dimethoxy-9-[(trimethylsilyl)oxy]benzocycloheptene-5-carboxylate (3e). 2e (0.390 g, 2 mmol), rhodium(II) pivalate, hexane, silica, diethyl ether/ petroleum ether (1:9); yield 0.459 g (62%) of a colorless oil: IR (neat) 2940, 2880, 2840, 2820, 1700, 1650, 1440, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.85 (dd, 1 H, J = 9.8, 3.7 Hz), 4.17 (q, 2 H, J = 7.2 Hz), 3.46 (s, 3 H), 3.26 (m, 1 H), 3.19 (s, 3 H), 2.84 - 1.34 (m, 10 H), 1.28 (t, 3 H, J = 7.2 Hz), 0.13 (s, 9 H); MS m/e (relative intensity) 368 (18), 336 (5), 307 (20), 263 (36), 191 (15), 149 (10), 119 (11), 73 (100); HRMS calcd for $C_{19}H_{32}O_5Si$ 368.2019, found: 368.2024.

Dimethylethyl 4,5-Dimethoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (3f). 2f (0.42 g, 2.5 mmol), rhodium(II) octanoate, hexane, silica, diethyl ether/ petroleum ether (1:4); yield 0.514 g (60%) of a colorless oil: IR (neat) 2960, 2820, 1700 br, 1640, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.81 (apparent t, 1 H, J = 6.6 Hz), 4.64 (apparent t, 1 H, J = 6.6 Hz), 3.48 (s, 3 H), 3.28 (s, 3 H), 3.14 (dd, 1 H, J = 17.0, 6.4 Hz), 3.00 (dd, 1 H, J = 17.0, 6.1 Hz), 2.76 (dd, 1 H, J = 17.0, 7.1 Hz), 2.58 (dd, 1 H, J = 17.0, 6.4 Hz), 1.47 (s, 9 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 165.7, 155.7, 137.5, 135.6, 98.5, 98.0, 80.2, 53.7, 49.7, 37.8, 28.0, 22.5, 1.5; MS m/z (relative intensity) 342 (85), 329 (100), 317 (30), 285 (40), 272 (45), 255 (60); HRMS Calcd for $C_{17}H_{30}O_5Si$ 342.1863, found 342.1872.

Methyl 3,4,5-Trimethoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (3h). 6 (1.50 g, 8.71 mmol) was converted to **2h** by the published procedure.[19] After rapid purification by chromatography on silica using diethyl ether/ hexane (1:19) as eluant, the vinyldiazomethane fraction was concentrated to 100 mL, and then added over a 10 min period to a solution of **2** (8.80 g, 44 mmol) and rhodium(II) pivalate (0.0517 g, 0.0871 mmol) in hexanes (50 mL) using the general procedure. Silica, diethyl ether/ petroleum ether (1:9), yield 0.89 g (31%) of a colorless oil: IR (neat) 2950, 2900, 2820, 1705, 1650, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (d, 1 H, J= 6.1 Hz), 4.84 (t, 1 H, J= 6.1 Hz), 4.00 (d, 1 H, J= 6.1 Hz), 3.73 (s, 3 H), 3.47 (s, 3 H), 3.41 (s, 3 H), 3.23 (s, 3 H), 3.23 (dd, 1 H, J= 18.8, 6.1 Hz), 3.09 (dd, 1 H, J= 18.8, 6.1 Hz), 0.11 (s, 9 H); MS m/e (relative intensity); 330 (16), 283 (10), 209 (8), 191 (30), 167 (37), 151 (20), 135 (14), 89 (40), 73 (100); HRMS calcd for $C_{15}H_{26}O_6Si$ 330.1499, found 330.1482

Diethyl 4-Hydroxy-5-methoxycyclohepta-1,3,5-triene-1,3-dicarboxylate (4a). A solution of **3a** (0.7739 g, 2 mmol) and 10% HCl (10 mL) in THF (10 mL) was stirred at room temperature for 1 h. The mixture was poured onto water and extracted with diethyl ether. The organic portion was dried ($MgSO_4$) and concentrated. Purification by chromatography on silica using diethyl ether as eluant afforded **4a** as a white solid: mp 90-92 °C; 0.444 g (79% yield); IR ($CHCl_3$) 1695, 1650, 1550, 1465, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.6 (s, 1 H), 7.40 (s, 1 H), 5.23 (t, 1 H, J = 7.9 Hz), 4.29 (q, 2 H, J = 7.1 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 3.56 (s,

3 H), 2.63 (d, 2 H, J = 7.9 Hz), 1.31 (t, 3 H, J = 7.1 Hz), 1.26 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 172.1, 168.9, 165.9, 150.8, 130.4, 125.4, 106.7, 104.9, 62.0, 60.7, 56.1, 21.9, 14.3, 14.2. Anal. Calcd for $C_{14}H_{18}O_6$ C, 59.57; H, 6.43. Found: C, 59.45; H, 6.45.

2,4-Bis(ethoxycarbonyl)-7-methoxycyclohepta-2,4,6-trien-1-one (5a). A stirred solution of **4a** (0.399 g, 1.5 mmol) and DDQ (0.38 g, 1.65 mmol) in benzene (25 mL) was heated under reflux for 24 h. The mixture was concentrated and the product was purified by chromatography on silica using diethyl ether/ petroleum ether(4:1) as eluant to afford **5a** as a white solid: mp 142-144 °C; 0.366 g (84% yield); ^{1}H NMR ($CHCl_3$) δ 8.26 (d, 1 H, J = 1.7 Hz), 8.10 (dd, 1 H, J = 10.3, 1.7 Hz), 6.70 (d, 1 H, J = 10.3 Hz), 4.33 (q, 2 H, J = 7.1 Hz), 4.31 (q, 2 H, J = 7.1 Hz), 3.96 (s, 3 H), 1.35 (t, 3 H, J = 7.1 Hz), 1.31 (t, 3 H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 177.3, 168.3, 167.7, 165.6, 138.7, 137.7, 134.8, 127.1, 109.8, 62.2, 62.0, 57.2, 14.3, 14.1; MS m/e (relative intensity) 280 (9), 251 (100), 223 (43), 207 (32), 179 (33), 149 (13), 121 (8), 95 (8), 77 (12), 58 (24). Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75. Found: C, 59.91; H, 5.70.

Oxidation of Cycloheptadiene 3 to 2-Methoxytropones 5. General Procedures. Method A. A stirred solution of **3** (4 mmol), DDQ (5 mmol) and p-toluenesulfonic acid monohydrate (1 mmol) in benzene (75 mL) and water (10 mL) was heated under reflux for 2-12 h. The mixture poured onto water and extracted with ethyl acetate. The organic portion was dried ($MgSO_4$) and concentrated.

Method B. A solution of **3** (1 mmol) and citric acid (3 mmol) were stirred in THF (10 mL) and water (10 mL) for 2 h. The mixture was poured onto water and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$) and concentrated to provide crude **4** as an oil. The crude **4** was stirred with DDQ (0.908 g, 4.0 mmol) in benzene (20 mL) for 96 h.

5-[(Dimethylethoxy)carbonyl]-2-methoxy-7-phenylcyclohepta-2,4,6-trien-1-one (5b). Method A, **3b** (1.768 g, 4.22 mmol), purification by chromatography on silica using ethyl acetate as eluant afforded pure **5b** as a colorless solid: 1.21 g (91% yield); IR ($CHCl_3$) 2980, 1700, 1590, 1410 cm^{-1}; ^{1}H NMR (benzene-d_6) δ 8.56 (d, 1 H, J = 1.7 Hz), 7.93 (dd, 1 H, J = 10.2, 1.7 Hz), 7.72 (br d, 2 H, J = 7.0 Hz), 7.37-7.25 (m, 3 H), 6.00 (d, 1 H, J = 10.2 Hz), 3.30 (s, 3 H), 1.57 (s, 9 H). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.95; H, 6.50.

5-(Ethoxycarbonyl)-2-methoxy-7-(phenylthio)cyclohepta-2,4,6-trien-1-one (5c). 2c (1.26 g, 5 mmol) was converted to **3c** using rhodium(II) pivalate/hexane as described in the general procedure. Unpurified **3c**, Method A, purification by chromatography on silica using ether as eluant afforded **5c** as a yellow solid: mp 158-160 °C; 0.729 g (46% yield); IR ($CHCl_3$) 1710, 1530, 1430, 1330 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.93 (dd, 1 H, J= 10.6, 1.4 Hz), 7.62 (d, 1 H, J= 1.4 Hz), 7.59-7.49 (m, 5 H), 6.89 (d, 1 H, J= 10.6 Hz), 4.15 (q, 2 H, J= 7.1 Hz), 4.03 (s, 3 H), 1.15 (t, 3 H, J= 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 175.1, 166.1, 161.7, 153.7, 136.3, 132.1, 131.0, 130.1, 130.0, 128.5, 126.7, 111.9, 61.8, 56.9, 13.9; MS m/e (relative intensity) 316 (43), 281 (24), 243 (12), 207 (100), 177 (35), 149 (20), 110 (25), 96 (23), 55 (21). Anal. Calcd for $C_{17}H_{16}O_4S$: C,64.54; H, 5.10. Found: C, 64.66; H, 5.17.

2,3-Dihydro-5-methoxy-8-(methoxycarbonyl)-4(1*H*)-azulenone (5d). **3d** (0.544 g, 1.6 mmol), method A, purification by chromatography on silica using ether/ petroleum ether (1:1), then (1:1) ether/ dichloromethane as eluant afforded **5d**: mp 92-95 °C; 0.301 g (80% yield); IR ($CHCl_3$) 1705, 1570, 1500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.67 (d, 1 H, J= 10.7 Hz), 6.65 (d, 1 H, J= 10.7 Hz), 3.94 (s, 3 H), 3.85 (s, 3 H), 3.27 (t, 2 H, J = 7.6 Hz), 3.09 (t, 2 H, J = 7.6 Hz), 1.89 (pentet, 2 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 176.9, 168.2, 164.9, 151.3, 149.0, 134.1, 129.3, 109.5, 56.4, 52.5, 39.5, 36.4, 22.0; MS m/e (relative intensity) 234 (100), 205 (38), 191 (30), 173 (43), 147 (64), 131 (20), 115 (51), 103 (30), 77 (32). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.77; H, 6.04.

9-(Ethyoxycarbonyl)-1,2,3,4-tetrahydro-6-methoxy-5*H*-benzocyclohepten-5-one (5e). **3e** (0.3682 g, 1 mmol) method B, purification by chromatography on silica using ether/ petroleum ether (1:1) as eluant afforded **5e** as a colorless solid: 0.155 g (59% yield); IR (neat) 2880, 2820, 2800, 1680, 1555, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.04 (d, 1 H, *J* = 9.8 Hz), 6.42 (d, 1 H, *J* = 9.8 Hz), 4.30 (q, 2 H, *J* = 7.2 Hz), 3.85 (s, 3 H), 2.79 (t, 2 H, *J* = 5.7 Hz), 2.68 (t, 2 H, *J* = 5.5 Hz), 1.73-1.63 (m, 4 H), 1.34 (t, 3 H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 182.0, 169.5, 162.0, 144.9, 142.5, 135.3, 128.5, 107.8, 61.6, 56.4, 31.1, 28.2, 21.6, 21.3, 14.2; MS m/e (relative intensity) 262 (100), 233 (64), 217 (14), 187 (34), 173 (20), 149 (17), 129 (24), 105 (14), 70 (35). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.71; H, 6.91.

5-[(Dimethylethoxy)carbonyl]-2-methoxycyclohepta-2,4,6-trien-1-one (5f). **3f** (0.3425 g, 1 mmol), method A, purification by chromatography on silica using ether/ petroleum ether (1:1), then (1:1) ether/ dichloromethane as eluant afforded **5f** as a white solid: mp 92-95 °C; 0.142 g (60% yield); IR ($CHCl_3$) 2960, 1720, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (dd, 1 H, *J* = 10.5, 1.8 Hz), 7.87 (dd, 1 H, *J*= 12.7, 1.8 Hz), 7.16 (d, 1 H, *J* = 12.7 Hz),6.71 (d, 1 H, *J* = 10.5 Hz) 3.95 (s, 3 H), 1.53 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 179.9, 167.0, 164.8, 136.0, 135.1, 130.1, 110.4, 82.2, 56.5, 27.9; MS m/e (relative intensity) 236 (15), 180 (100), 151 (63), 135 (41), 107 (19), 105 19), 77 (13), 57 (25). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.07; H, 6.83. Found: C,65.96; H, 6.82.

2-Methoxy-5-(methoxycarbonyl)-7-methylcyclohepta-2,4,6-trien-1-one (5g). **2g** (0.28 g, 2 mmol) was converted to **3g** using rhodium(II) pivalate. Unpurified **3g**, method A, purification by chromatography on silica using ether/ dichloromethane (4:1) as eluant afforded **5g** as a white solid: mp 118-120 °C; 0.278 g (67% yield); IR ($CHCl_3$) 1700, 1570, 1500, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.12 (br s, 1 H), 7.97 (d, 1 H, *J*= 10.5 Hz), 6.72 (d, 1 H, *J*= 10.5 Hz), 3.96 (s, 3 H), 3.89 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 179.6, 167.0, 165.2, 145.1, 134.5, 134.0, 127.3, 110.0, 56.6, 52.8, 23.7; MS m/e (relative intensity) 208 (100), 193 (10), 179 (45), 149 (100), 147 (34), 121 (39), 105 (29), 91 (54), 77 (46). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.23; H, 5.77.

2,7-Dimethoxy-5-(methoxycarbonyl)cyclohepta-2,4,6-trienone (5h). **3h** (0.660 g, 2 mmol), method A, purified by chromatography on alumina using ether/ petroleum ether (1:1) as eluant to afford **5h** as a colorless solid: 0.262 g (58% yield); IR (neat) 2900, 2840, 1700, 1575, 1550, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86 (dd, 1 H, *J* = 10.4, 1.3 Hz), 7.64 (d, 1 H, *J* = 1.3 Hz), 6.85 (d, 1 H, *J* = 10.4 Hz), 3.96 (s, 6 H), 3.91 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.7, 167.0, 160.2, 129.1, 126.1, 112.4, 111.6, 56.7, 56.5, 53.0, one signal superimposed; MS m/e (relative intensity) 224 (87), 209 (100), 179 (68), 165 (30), 149 (16), 135 (20), 107 (21), 91 (13), 79 (59). Anal. Calcd for $C_{11}H_{12}O_5$: C,58.93; H, 5.39. Found: C, 59.04; H, 5.37.

Synthesis of 3-Methoxytropones (9). General Procedure. A stirred solution of **2** (5 mmol) in hexane (10 mL) was added over a 10 min period to stirred solution of **7** (2.02 g, 10 mmol) and rhodium(II) pivalate dimer (0.0323 g, 0.05 mmol) in hexane (10 mL), heated under reflux in a an argon atmosphere. The resulting solution was refluxed for an additional 10 min, concentrated, and the excess diene was removed by Kugelrohr distillation to provide crude **3** as an unstable oil. The crude **3** and $VO(OR)Cl_2$[21,22] (15.0 mmol) in methanol (25 mL) were heated under reflux for 30 min. Ten drops of conc HCl was then added and the mixture was poured onto saturated sodium chloride solution and extracted twice with diethyl ether. The ether extracts were dried ($MgSO_4$), concentrated and the residue was purified by chromatography on silica using ether/ petroleum ether mixtures as eluant. The scale of reaction, the vanadyl reagent and chromatographic solvent used are presented in that order in abbreviated format.

5-(Ethyoxycarbonyl)-3-methoxy-7-(phenylthio)cyclohepta-2,4,6-trien-1-one (9c) and 5-(Ethoxycarbonyl)-3-methoxy-5-[(2-phenylthio)-1-ethenyl]cyclopent-2-en-1-one (10). **2c** (0.50 g, 2 mmol), $VO(OiPr)Cl_2$,[22] diethyl ether: gave two compounds: **9c**: yield 0.067 g (11%); mp 162-164 °C; IR ($CHCl_3$) 1700, 1580, 1500, 1450, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60-7.49 (m, 6 H), 7.19 (d, 1 H, *J*= 1.4 Hz), 6.66 (d, 1 H, *J*= 2.7 Hz), 4.16 (q, 2 H, *J*= 7.1 Hz), 3.82 (s, 3 H), 1.17 (t, 3 H, *J*= 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 180.4, 165.6, 164.6, 159.5, 136.1, 130.9, 130.6, 130.2, 130.1, 130.1, 123.8, 115.2, 62.3, 56.1, 13.9; MS m/e (relative intensity) 316 (100), 288 (87), 260 (11), 243 (29), 200 (48), 171 (23), 144 (13), 110 (28), 77 (15), 69 (21); HRMS calcd for $C_{17}H_{16}O_4S$: 316.0769, found: 316.0793.

10: yield 0.488 g (77%); IR (neat) 3080, 3040, 2975, 2920, 2880, 2840, 1690, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) E/Z ratio 1 : 4; E isomer δ 7.30-7.19 (m, 5 H), 6.44 (d, 1 H, *J*= 9.7 Hz), 6.22 (d, 1 H, *J*= 9.7 Hz), 5.28 (br s, 1 H), 4.18 (q, 2 H, *J*= 7.1 Hz), 3.87 (s, 3 H), 3.56 (d, 1 H, *J*= 17.6 Hz), 2.91 (d, 1 H, *J*= 17.6 Hz), 1.22 (t, 3 H, *J*= 7.1 Hz). Z isomer δ 7.30-7.19 (m, 5 H), 6.41 (d, 1 H, *J*= 15.5 Hz), 6.19 (d, 1 H, *J*= 15.5 Hz), 5.22 (br s, 1 H), 4.17 (q, 2 H, *J*= 7.1 Hz), 3.86 (s, 3 H), 3.31 (d, 1 H, *J*= 17.7 Hz), 2.73 (d, 1 H, *J*= 17.7 Hz), 1.24 (t, 3 H, *J*= 7.1 Hz); ^{13}C NMR ($CDCl_3$) Z isomer δ 199.2, 190.6, 169.3, 135.1, 129.9, 129.3, 129.1, 129.0, 128.0, 127.1, 101.4, 62.4, 59.2, 39.3, 14.0; MS m/e (relative intensity) 318 (59), 273 (2), 245 (56), 209 (100), 181 (30), 136 (61), 109 (46), 77 (18), 69 (45). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 63.99; H, 5.78.

3-Methoxy-5-(methoxycarbonyl)-7-methylcyclohepta-2,4,6-trien-1-one (9g). **2g** (0.282 g, 2 mmol), $VO(OiPr)Cl_2$,[22] ether/petroleum ether (1:1); yield 0.243 g (58%) of a white solid: mp 96-98 °C; IR ($CHCl_3$) 1700, 1600, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74 (br s, 1 H), 7.64 (br s, 1 H), 6.53 (d, 1 H, *J* = 2.9 Hz), 3.88 (s, 3 H), 3.75 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 184.9, 166.5, 163.6, 150.7, 134.0, 131.7, 130.0, 118.4, 55.8, 53.2, 23.1; MS m/e (relative intensity) 208 (35), 180 (51), 149 (100), 121 (44), 106 (8), 91 (22), 77 (19). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.54; H, 5.85.

3-Methoxy-5-(methoxycarbonyl)-7-phenylcyclohepta-2,4,6-trien-1-one (9i). **2i** (1.01 g, 5 mmol), $VO(OEt)Cl_2$,[21] ether/petroleum ether (1:4); yield 0.839 g (62%) of a yellow solid: mp 128-130 °C; IR ($CHCl_3$) 1715, 1630, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, 1 H, *J* = 1.4 Hz), 7.73 (dd, 1 H, *J* = 2.9, 1.4 Hz), 7.49-7.36 (m, 5 H), 6.66 (d, 1 H, *J* = 1.4 Hz), 3.91 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 183.7, 165.9, 162.9, 151.1, 139.5, 134.5, 131.4, 131.1, 128.6, 128.1, 127.7, 119.9, 55.6, 52.9.; MS m/e (relative intensity) 270 (59), 242 (74), 211 (100), 168 (59), 152 (23), 139 (54), 105 (22), 77 (31), 69 (28). Anal. Calcd for $C_{16}H_{14}O_4$: C,71.10; H, 5.22. Found: C, 71.00; H, 5.28.

3-(Ethylthio)-7-methoxy-5-(methyoxycarbonyl)cyclohepta-2,4,6-trien-1-one (9j). **2j** (0.92 g, 5 mmol) $VO(OiPr)Cl_2$,[22] diethyl ether; yield 0.495 g (39%) of a yellow solid: mp 110-112 °C; IR ($CHCl_3$) 1710, 1560, 1500, 1400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 (dd, 1 H, *J*= 2.9, 1.3 Hz), 7.56 (br s, 1 H), 6.59 (d, 1 H, *J*= 2.9 Hz), 3.93 (s, 3 H), 3.80 (s, 3 H), 2.89 (q, 2 H, *J*= 7.4 Hz), 1.42 (t, 3 H, *J*= 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 181.0, 166.7, 164.4, 157.5, 130.4, 129.5, 122.2, 114.7, 56.1, 53.4, 25.7, 12.1; MS m/e (relative intensity) 254 (100), 221 (41), 198 (9), 193 (48), 167 (17), 135 (29), 123 (10), 95 (13), 69 (24), 59 (19). Anal. Calcd for $C_{12}H_{14}O_4S$: C,56.68; H, 5.55. Found: C, 56.49; H, 5.54.

3-Methoxy-5-(methoxycarbonyl)-5-[(2-(Z)-methoxy)ethenyl]cyclopent-2-en-1-one (11). **6** (1.50 g, 8.71 mmol) was converted to **2h** by the published procedure.[19] After rapid purification by chromatography on silica using diethyl ether/ hexane (1:19) as eluant, the vinyldiazomethane fraction was concentrated to 100 mL, and then added over a 10 min period to a solution of **7** (8.80 g, 44 mmol) and rhodium(II) pivalate dimer (0.0563 g, 0.0871 mmol) in hexanes (50 mL) using the general procedure. Diethyl ether/ petroleum ether (1:9); yield 0.624 g (32%) of a colorless oil: IR (neat) 3080, 2940, 2840, 1720, 1690, 1660, 1600, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.99 (d, 1 H, *J*= 6.4 Hz), 5.23 (s, 1 H), 4.89 (d, 1 H, *J*= 6.4 Hz), 3.86 (s, 3 H), 3.69 (s, 3 H), 3.55 (s, 3 H), 3.39 (d, 1 H, *J*= 17.6 Hz), 2.87 (d, 1 H, *J*= 17.6 Hz); ^{13}C NMR

($CDCl_3$) δ 200.2, 190.6, 170.8, 148.4, 103.7, 101.0, 59.9, 58.9, 58.5, 53.0, 40.6; MS m/e (relative intensity) 226 (35), 184 (20), 167 (60), 152 (6), 139 (12), 125 (50), 95 (21), 95 (21), 75 (100); HRMS calcd for $C_{12}H_{14}O_5$ 226.0841, found 226.0840

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