Versatile Synthesis of Tropones by Reaction of Rhodium(II)-Stabilized Vinylcarbenoids with 1-Methoxy-1-[(trimethylsilyl)oxy]buta-1,3-diene

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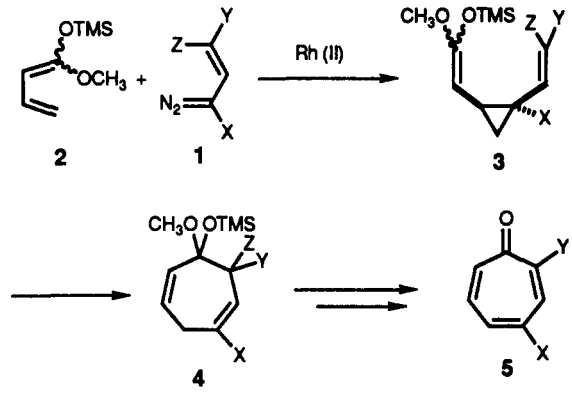
Received June 24, 1991

Rhodium(II)-catalyzed decomposition of vinyldiazomethanes in the presence of 1-methoxy-1-[(trimethylsilyl)oxy]buta-1,3-diene leads to [3 + 4] annulation products by a tandem cyclopropanation/Cope rearrangement sequence. The resulting cycloheptadienes are readily converted to cycloheptatrienones either by hydrolysis with mild acid followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or by treatment with dichloroethoxyoxovanadium. The efficiency of the general strategy was demonstrated through a short synthesis of nezukone.

The tropone ring has aroused considerable interest due to its novel structure, its presence in a number of potent natural products,[1-6] and more recently, its utility in novel synthetic strategies.[7-13] Consequently, over the last 40 years, a large number of ingenious and elaborate approaches to this ring system have been developed.[14-25]

Scheme I



Many of the earlier schemes involved expansion of six-membered rings, but in recent years significant advances have been reported based on concerted reactions. These include two [3 + 4] cycloaddition strategies using either allyl cations[25] or a nucleophilic vinylcarbene[24] as the key intermediates, [5 + 2] cycloadditions between heterocyclic betaines and alkenes,[22] and Cope rearrangements of divinylcyclopropanes.[23] The synthesis of functionalized tropones has not been completely solved, however, because many of these processes are not really general and succinct.

We now report an alternative and flexible [3 + 4] annulation strategy for the synthesis of tropones based on the rhodium(II)-catalyzed decomposition of vinyldiazomethanes (1) in the presence of 1-methoxy-1-[(trimethylsilyl)oxy]buta-1,3-diene (2). In earlier studies to explore the synthetic potential of vinylcarbenoids, we have shown that their reaction with furans,[26] pyrroles,[27] and

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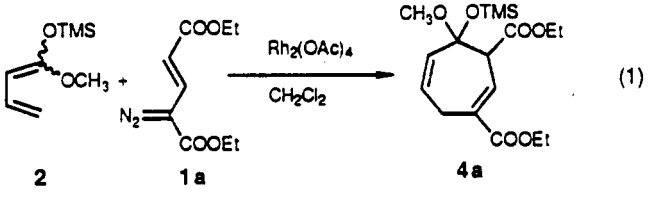
Table I. Synthesis of Oxygenated Cycloheptadienes (4)

substrate	X	Y	Z	catalyst	solvent	product	yield, %
1a	COOEt	COOEt	H	$Rh_2(OAc)_4$	CH_2Cl_2	4a	87
1b	COOMe	Ph	H	$Rh_2(OAc)_4$	CH_2Cl_2	4b	73
1c	COOEt	CH=CHPh	H	$Rh_2(OAc)_4$	CH_2Cl_2	4c	89
1d	COOEt	SO_2Ph	H	$Rh_2(Piv)_4$	pentane	4d	79
1e	SO_2Ph	COOEt	H	$Rh_2(Piv)_4$	pentane	4e	58
1f	COOEt	COOEt	OCH_3	$Rh_2(Piv)_4$	heptane	4f	79
1g	COMe	Ph	H	$Rh_2(Piv)_4$	pentane	4g	71
1h	$COOBu^t$	H	H	$Rh_2(Piv)_4$	pentane	4h	74
1i	COOMe	H	H	$Rh_2(Piv)_4$	pentane	4i	67
1j	COOEt	$CH=CH_2$	H	$Rh_2(Piv)_4$	pentane	4j	89

dienes,[28] both inter- and intramolecularly, offers an excellent entry to highly functionalized seven-membered rings. The reaction proceeds by a tandem cyclopropanation/Cope rearrangement mechanism. Extension of this chemistry to oxygenated dienes would be expected to allow ready access to tropone derivatives (5) as illustrated in Scheme I. Although mechanistically quite distinct, this strategy compliments the concerted [3 + 4] cycloaddition using a nucleophilic vinylcarbene developed by Boger and Brotherton.[24] The scheme would proceed through a Cope rearrangement of divinylcyclopropanes 3, but unlike the earlier approach to tropones using a Cope rearrangement, described by Wenkert,[23] the synthesis of the *cis*-divinylcyclopropanes should be very practical and direct.

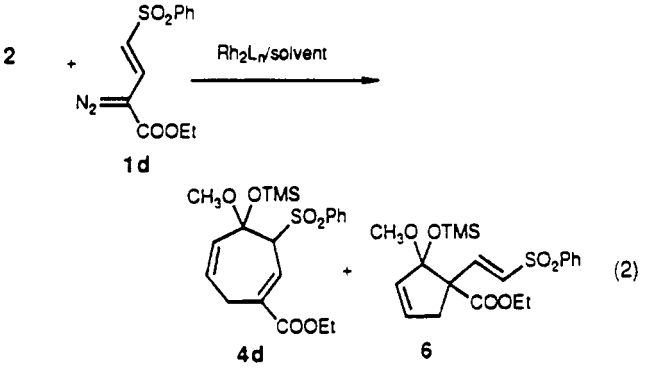
Results

In order for the reaction of rhodium-stabilized vinylcarbenoids with oxygenated dienes to effectively generate seven-membered rings, several potential problems need to be controlled. The initial cyclopropanation must be both regio- and stereoselective, side reactions due to dipolar intermediates need to be inhibited, and steric factors must be minimized to avoid suppression of the Cope rearrangement.[29] Considering all these factors, the result of the rhodium(II) acetate catalyzed decomposition of the vinyldiazomethane 1a in the presence of 2 equiv of an isomeric mixture of 1-methoxy-1-[(trimethylsilyl)oxy]butadiene (2) was very promising. The cycloheptadiene system 4a was cleanly formed in 87% yield as a mixture of diastereomers (eq 1). The regiochemistry was readily determined from the ^1H NMR spectrum as the methylene group was a doublet. This result is consistent with initial cyclopropanation at the more sterically accessible double bond, followed by a Cope rearrangement of the resulting divinylcyclopropane. Furthermore, the high yield of 4a would indicate that the cyclopropanation was much more stereoselective, favoring the *cis*-divinylcyclopropane, than the corresponding reactions with alkyl-substituted dienes.[28c]



2 1a 4a (1)

Similar reactions were observed in the reactions of 1b and 1c, in which the γ-ester group had been replaced by either phenyl or styryl (Table I). The formal [3 + 4] cycloadducts 4b and 4c were cleanly formed in 73% and 89% yield, respectively. In contrast, side reactions were observed with 1d, in which the γ-ester group had been replaced by phenylsulfonyl. The predominant product in the rhodium(II) acetate catalyzed decomposition of 1d in the presence of 2 with dichloromethane as solvent was the formal [1 + 4] cycloadduct 6 (47% yield), and only a small amount of the formal [3 + 4] cycloadduct 4d (23%) was obtained (eq 2). The formal [1 + 4] cycloadduct probably arose by means of dipolar intermediates, and so, inhibition of its formation was expected by use of nonpolar solvents. Indeed, decomposition of 1d with rhodium(II) pivalate and pentane as solvent totally suppressed the formation of 6 and produced the formal [3 + 4] cycloadduct 4d in 79% yield. The isomeric vinyldiazomethane 1e also gave a cycloheptadiene (4e) in 58% yield on rhodium(II) pivalate catalyzed decomposition in the presence of the diene 2 in pentane.



(2)

		4d	6
$Rh_2(OAc)_4$	CH_2Cl_2	23%	47%
$Rh_2(OPiv)_4$	Pentane	79%	0%

Side reactions were prevalent in the rhodium(II) acetate catalyzed decomposition of the sterically crowded vinyldiazomethane 1f. When dichloromethane was used as solvent, none of the desired [3 + 4] cycloadduct 4f was formed, but instead, a mixture of the formal [1 + 4] cycloadduct 7 and the acyclic product 8 was obtained (eq 3). In certain regards, this result was surprising because the methoxy group would be expected to disfavor dipolar intermediates but the additional steric hindrance would also inhibit the Cope rearrangement. Once again, however, modification of reaction conditions to rhodium(II) pivalate in heptane caused a complete change in product distribution, and 4f was obtained in 79% yield.

Reaction conditions were also crucial in the decomposition of 1g in which the α-ester was replaced by a keto group. None of the formal [3 + 4] cycloadduct was formed from the rhodium(II) acetate catalyzed reaction in di-

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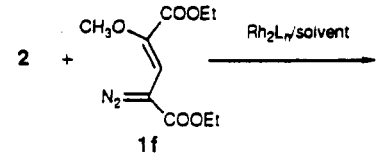
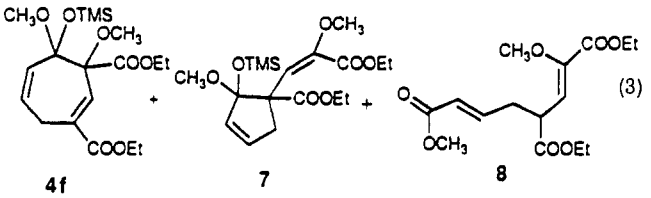
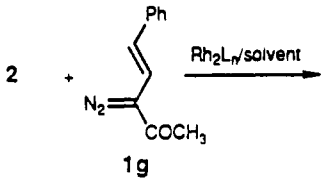


1f

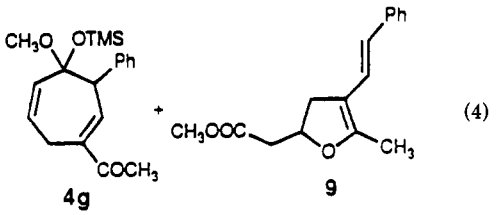


	4f	7	8
$Rh_2(OAc)_4$ CH_2Cl_2	0	18%	50%
$Rh_2(OPiv)_4$ Pentane	79%	0	0

chloromethane, and instead, the dihydrofuran **9** was isolated in 35% yield after an aqueous workup (eq 4).[30] The formation of the formal [2 + 3] cycloadduct **9** could be suppressed by using rhodium(II) pivalate in pentane. Under these conditions, the cycloheptadiene **4g** was cleanly produced in 71% yield.



1g



	4g	9
$Rh_2(OAc)_4$ CH_2Cl_2	0%	35%
$Rh_2(OPiv)_4$ Pentane	71%	0%

We have recently demonstrated that the tandem cyclopropanation/Cope rearrangement sequence can be extended to vinylcarbenoids with only a single electron-withdrawing group.[31] In this case, it was necessary to inhibit electrophilic reactivity at the vinylogous position of the carbenoid, and this was achieved by using nonpolar solvents and electron-releasing ligands on the rhodium catalyst. Similar reactivity was observed in the decomposition of **1h–j** with rhodium(II) pivalate with pentane as solvent in the presence of the diene **2**, as the formal [3 + 4] cycloadducts **4h–j** were readily formed (Table I).

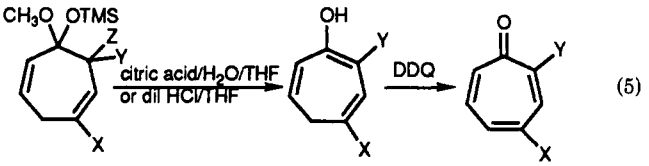
Through the appropriate choice of conditions, ready access to a series of cycloheptadienes (**4**) was achieved.

Table II. Preparation of Tropones (5) from Oxygenated Cycloheptadienes (4) by Hydrolysis Followed by Oxidation with DDQ

substrate	hydrolysis conditns	10 (yield, %)	5 (yield, %)
4a	citric acid/H_2O/THF	**10a** (100)	**5a** (92)
4b	citric acid/H_2O/THF	**10b** (97)	**5b** (98)
4c	citric acid/H_2O/THF	**10c** (97)	**5c** (22)
4d	HCl/H_2O/THF		**5d** (76)[a]
4e	HCl/H_2O/THF	**10e** (75)	**5e** (65)
4g	citric acid/H_2O/THF	**10g** (76)	**5g** (69)
4h	citric acid/H_2O/THF		**5h** (47)[a]

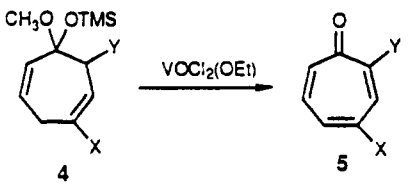
[a] Intermediate **10** was unstable, and the value represents the overall yield for conversion of **4** to **5**.

Further modification of **4** to tropones (**5**) required hydrolysis and oxidation, and it was envisioned that this could be achieved by conventional approaches. In the case of systems with two electron-withdrawing groups, **4a–c,g**, a short exposure to aqueous citric acid generated the cycloheptatrienols **10a–c,g** in high yield (eq 5, Table II). In the case of **4d** and **4e**, 20% hydrochloric acid was required for complete conversion to the cycloheptatrienols **10d** and **10e**. Hydrolysis of **4h** was only moderately successful, which was due to the instability of cycloheptatrienols functionalized with a single electron-withdrawing group. Completion of the tropone synthesis was readily achieved by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of **10a,b,d,e,g,h** to **4a,b,d,e,g,h** (Table II). A similar oxidation with the vinyl derivative **10c**, however, was not a clean process, which was probably due to competing oxidation of the vinyl group.



4 10 5

Due to the difficulties observed in isolation of the cycloheptadienones containing a single electron-withdrawing group in the 4-position, attempts were made to develop a process whereby the hydrolysis and oxidation occurred under the same reaction conditions. A reagent that seemed ideal in this regard was $VO(OEt)Cl_2$, which has been used to aromatize cyclohexenone derivatives.[32] Not only would $VO(OEt)Cl_2$ behave as a Lewis acid capable of releasing the protected carbonyl but also it is an effective oxidizing agent under very mild conditions. Upon treatment of **4h** with $VO(OEt)Cl_2$ in refluxing ethanol, the desired hydrolysis/oxidation occurred to afford the tropone **5h** in 47% yield (eq 6). Similar reactions with **4b** and **4i** resulted in the formation of **5b** and **5i**.



4 5

X	Y	Product
COO^tBu	H	**5h** (47%)
COOMe	Ph	**5b** (71%)
COOMe	H	**5i** (54%)

(30) For earlier examples of dihydrofuran formation in carbenoid reactions, see: (a) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sanchez, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2021. (b) Alonso, M. E.; Jano, P.; Hernandez, M.; Greenberg, R. S.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 3047. (c) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem.* **1982**, *47*, 3747. (d) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Chou, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 4778. (e) Graziano, M. L.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 289.

(31) Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299.

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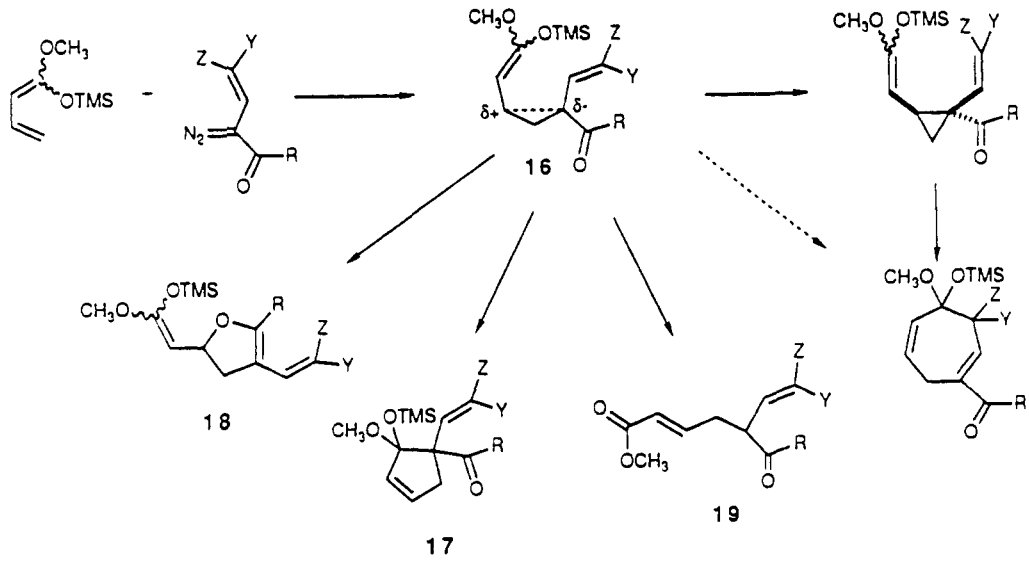
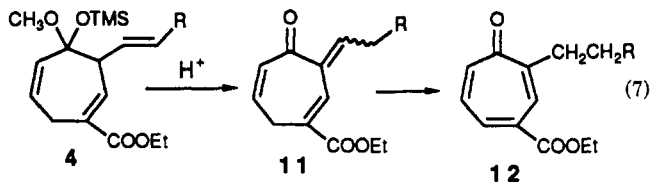
Scheme II

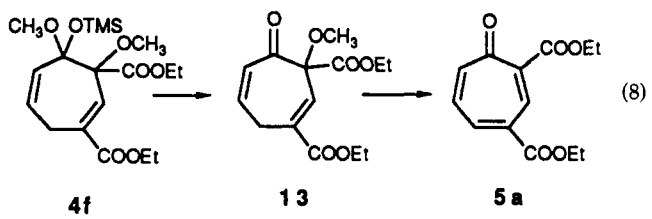


An alternative approach to generate the tropone system was developed by the use of appropriate functionality that would allow aromatization to occur, through either elimination or equilibration, without the need for an oxidation step. Such functionality was present in the cycloheptadienes **4c**, **4f**, and **4j**. Hydrolysis of **4j** with citric acid caused migration of the vinyl group into conjugation, which resulted in the formation of **11j**. If more vigorous hydrolysis conditions were used, however, aromatization by isomerization of the exocyclic double bond occurred, to generate the 2-ethyltropone derivative **12j** (eq 7). In a similar manner, hydrolysis of **4c** with strong acid generated **12c** in 42% yield. An alternative entry to the tropone system was through elimination of the methoxy group in **13**. This was achieved by treatment of **4f** with citric acid, which resulted in the formation of **5a** (44% yield) by deprotection of the carbonyl and elimination of methanol (eq 8).



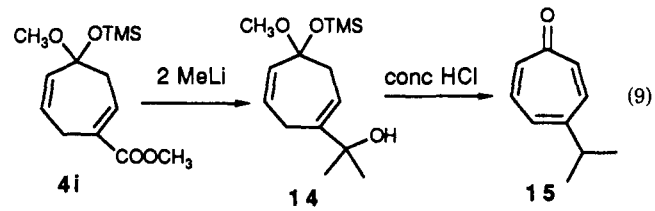
(7)

c: R = Ph
j: R = H



(8)

In order to demonstrate the potential of this approach to tropone structures, a short synthesis of nezukone was attempted, as shown in eq 9. Reaction of the cycloheptadiene **4i** with methyllithium generated the alcohol **14**. This step takes advantage of the stability of the carbonyl protecting group to basic conditions. Treatment of the crude material with concentrated hydrochloric acid generated nezukone (**15**) in 59% overall yield. The sequence compares very favorably with a previous synthesis of nezukone described by Wenkert,[23] which also involved the use of divinylcyclopropanes.



(9)

A particularly interesting feature of this chemistry was the dramatic effect of catalyst and solvent on the product distribution. The results could be rationalized by invoking the occurrence of a partially dipolar transition state caused by a nonsynchronous cyclopropanation step. In extreme cases, the cyclopropanation was not completed and side products derived from a dipolar structure (**16**) were observed (Scheme II). Nonpolar solvents would be expected to destabilize a polar transition state, and under these conditions, side reactions were totally suppressed and normal cyclopropanation/Cope rearrangements were observed. The positive end of the dipole would be strongly stabilized by the oxygen functionality of the diene, which explained why this anomalous behavior was not observed with alkyl dienes.[28c] The phenylsulfonyl group is excellent at stabilizing negative charge on the adjacent carbon, which would explain why the formal [1 + 4] cycloadduct (**17**) was formed with **1d**. A keto carbonyl is more nucleophilic than an ester group, and consequently, **1f** led to a dihydrofuran (**18**) in polar solvents. In certain respects the formation of side products (**17** and **19**) with the bulky vinyldiazomethane **1f** was rather unexpected. Considering that the diester **1a** led cleanly to a cycloheptadiene in polar solvents, similar reactivity would have been expected of **1f** because, on the basis of electronic effects, the methoxy group would be expected to destabilize the dipolar transition state. A possible explanation of the apparent anomalous reactivity of **1f** would be that partially dipolar structures could also be precursors to cycloheptadienes instead of the previously assumed divinylcyclopropanes. Consequently, even though the extent of dipolar character in the transition state should be less with the methoxy system (**1f**) than with the unsubstituted case (**1a**), steric hindrance would retard the Cope rearrangement, which would allow side reactions to dominate in a polar solvent.

In summary, the reaction between rhodium(II)-stabilized

vinylcarbenoids and 2 offers a direct synthetic approach to tropones. A whole range of functionality may be introduced if appropriate catalyst and solvent are used. The success of the process is based on the remarkable stereoselectivity of cyclopropanations by rhodium(II)-stabilized vinylcarbenoids.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh). The vinyldiazomethanes **1a–j** were prepared by methods that have been previously reported.[28] 1-Methoxy-1-[(trimethylsilyl)oxy]-buta-1,3-diene (**2**) was prepared by the method of Savard and Brassard.[33]

Rhodium(II) Acetate (or Pivalate) Catalyzed Decomposition of Vinyldiazomethanes 1 in the Presence of 2. General Procedure. A solution of **1** (1 equiv) in CH_2Cl_2 (10 mL) was added over 10–20 min to a stirred mixture of rhodium(II) acetate (0.01 equiv) and **2** (2–5 equiv) in CH_2Cl_2 (10 mL), heated under reflux in an argon atmosphere. Alternatively, a solution of **1** (1 equiv) in pentane–CH_2Cl_2 (9:1 to 19:1, 10–100 mL) was added to a stirred mixture of rhodium(II) pivalate (0.01 equiv) and **2** (2–5 equiv) in pentane (10–50 mL) under the same conditions. After heating for a further 10 min, the solvent was evaporated under reduced pressure and the excess diene was removed by Kugelrohr distillation (40–50 °C, 0.5 mmHg). The amounts of diazo compound (**1a–i**), diene, and rhodium(II) catalyst used are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parentheses.

Diethyl 4-methoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1,3-dicarboxylate (4a): 1a (1.06 g, 5.0 mmol), (1.72 g, 10 mmol), acetate (0.022 g, 0.05 mmol), (1:4); yield, 1.54 g (87%) of a colorless gum; 1:1 mixture of diasteromers; IR (neat) 2950, 2900, 2825, 1725 (sh), 1710, 1650, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10 (dd, 0.5 H, J = 6.9, 2.2 Hz), 7.06 (dd, 0.5 H, J = 6.8, 2.2 Hz), 5.97–5.82 (m, 1 H), 5.70 (dd, 0.5 H, J = 12.1, 2.5 Hz), 5.57 (dd, 0.5 H, J = 11.8, 3.0 Hz), 4.27–4.09 (m, 4 H), 3.96–3.91 (m, 1 H), 3.68–3.32 (m, 1 H), 3.29 (s, 1.5 H), 3.27 (s, 1.5 H), 3.16–2.99 (m, 1 H), 1.28 (t, 6 H, J = 7.1 Hz), 0.15 (s, 4.5 H), 0.11 (s, 4.5 H). Anal. Calcd for $C_{17}H_{28}O_6Si$: C, 57.28; H, 7.92. Found: C, 57.25; H, 7.93.

Methyl 4-methoxy-3-phenyl-4-[(trimethylsilyl)oxy]-cyclohepta-1,5-diene-1-carboxylate (4b): 1b (1.01 g, 5.0 mmol), (1.72 g, 10 mmol), acetate (0.022 g, 0.05 mmol), (1:6); yield, 1.26 g (73%) of a colorless gum; 1:1 mixture of diastereomers; IR (neat) 3060, 3020, 2960, 2900, 2820, 2820, 1700, 1650, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.26 (m, 5 H), 7.16 (dd, 0.5 H, J = 6.5, 2.1 Hz), 7.07 (dd, 0.5 H, J = 6.6, 2.2 Hz), 5.97 (m, 1 H), 5.71 (dd, 0.5 H, J = 12.0, 2.7 Hz), 5.58 (dd, 0.5 H, J = 11.6, 2.4 Hz), 4.08 (m, 1 H), 3.72 (s, 3 H), 3.28 (s, 1.5 H), 3.23 (s, 1.5 H), 3.60–3.10 (m, 2 H), –0.01 (s, 4.5 H), –0.06 (s, 4.5 H). Anal. Calcd for $C_{19}H_{26}O_4Si$: C, 65.86; H, 7.56. Found: C, 66.14; H, 7.35.

Ethyl 4-methoxy-3-(2-phenylethenyl)-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (4c): 1c (0.48 g, 2.0 mmol), (1.38 g, 8 mmol), acetate (0.0088 g, 0.02 mmol), (3:17); yield, 0.68 g (89%) of a yellow gum; 1:1 mixture of diastereomers; IR (neat) 3010, 2980, 2900, 2820, 1700, 1650, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.19 (m, 5 H), 7.03–6.95 (m, 1 H), 6.47–6.26 (m, 2 H), 5.91–5.59 (m, 2 H), 4.18 (br q, 2 H, J = 7.1 Hz), 3.74–3.57 (m, 2 H), 3.29 (s, 1.5 H), 3.26 (s, 1.5 H), 3.20–3.11 (m, 1 H), 1.29 (t, 3 H, J = 7.1 Hz), 0.18 (s, 4.5 H), 0.12 (s, 4.5 H). Anal. Calcd for $C_{22}H_{30}O_4Si$: C, 68.36; H, 7.82. Found: C, 68.76; H, 7.47.

Ethyl 4-methoxy-3-(phenylsulfonyl)-4-[(trimethylsilyl)-oxy]cyclohepta-1,5-diene-1-carboxylate (4d): 1d (1.34 g, 5.0 mmol), (3.30 g, 19 mmol), pivalate (0.0313 g, 0.05 mmol), (1:4); yield, 1.67 g (79%) of a yellow gum; 1:1 mixture of diastereomers; IR (neat) 3060, 2960, 2900, 1700, 1650, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88–7.82 (m, 2 H), 7.64–7.44 (m, 3 H), 7.01–6.91 (m, 1 H), 5.80–5.60 (m, 2 H), 4.55–4.48 (m, 1 H), 4.19 (q, 2 H, J = 7.1 Hz), 3.29–3.24 (m, 2 H), 3.10 (s, 1.5 H), 2.99 (s, 1.5 H), 1.28 (t, 3 H, J = 7.1 Hz), 0.06 (s, 4.5 H), 0.05 (s, 4.5 H). Although **4d** was spectroscopically pure, it was of insufficient stability to obtain an elemental analysis.

Ethyl 3-methoxy-4-[2-(phenylsulfonyl)-1-ethenyl]-3-[(trimethylsilyl)oxy]cyclopent-1-ene-4-carboxylate (6): 1d (0.84 g, 3.1 mmol), (1.72 g, 10 mmol), acetate (0.022 g, 0.05 mmol), (1:4); yield of **4d**, 0.49 g (23%); yield of **6**, 1.00 g (47%); 7:3 mixture of diastereomers; IR (neat) 3060, 2960, 2900, 1720, 1620, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89–7.84 (m, 2 H), 7.59–7.47 (m, 3 H), 7.37 (d, 0.3 H, J = 15.6 Hz), 7.26 (d, 0.7 H, J = 15.6 Hz), 6.40 (d, 0.7 H, J = 15.6 Hz), 6.31 (d, 0.3 H, J = 15.6 Hz), 6.11 (m, 0.3 H), 6.05 (m, 0.7 H), 5.72 (m, 0.3 H), 5.65 (m, 0.7 H), 4.13 (q, 2 H, J = 7.1 Hz), 3.35 (dt, 1 H, J = 17.4, 2.4 Hz), 3.24 (s, 0.9 H), 3.11 (s, 2.1 H), 2.39 (dt, 0.3 H, J = 17.4, 1.2 Hz), 2.35 (dt, 0.7 H, J = 17.4, 2.4 Hz), 1.23 (t, 3 H, J = 7.1 Hz), 0.09 (s, 6.3 H), 0.08 (s, 2.7 H). Anal. Calcd for $C_{20}H_{28}O_6SSi$: C, 56.58; H, 6.65. Found: C, 56.62; H, 6.68.

Ethyl 7-methoxy-3-(phenylsulfonyl)-7-[(trimethylsilyl)-oxy]cyclohepta-2,5-diene-1-carboxylate (4e): 1e (0.25 g, 0.93 mmol), (0.80 g, 4.65 mmol), pivalate (0.007 g, 0.01 mmol), (1:4); yield, 0.228 g (58%) of a colorless gum; 1:1 mixture of diastereomers; IR (neat) 3060, 2960, 2900, 2820, 1730, 1650, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.78 (m, 2 H), 7.58–7.44 (m, 3 H), 7.16 (br d, 1 H, J = 5.6 Hz), 5.72–5.50 (m, 2 H), 4.22–4.11 (m, 2 H), 4.10–3.91 (m, 1 H), 3.24 (s, 1.5 H), 3.19 (s, 1.5 H), 3.15–2.97 (m, 2 H), 1.25 (t, 1.5 H, J = 7.0 Hz), 1.21 (t, 1.5 H, J = 7.0 Hz), 0.10 (s, 4.5 H), 0.00 (s, 4.5 H). Anal. Calcd for $C_{20}H_{28}O_6SSi$: C, 56.58; H, 6.65. Found: C, 56.72; H, 6.71.

Diethyl 3,4-dimethoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1,3-dicarboxylate (4f): 1f (1.21 g, 5.0 mmol), (1.72 g, 10 mmol), pivalate (0.0323 g, 0.05 mmol), in heptane, heated under reflux, (1:4); yield, 1.54 g (79%) of a colorless gum; 1:1 mixture of diastereomers; IR (neat) 2980, 2900, 2820, 1730, 1700, 1645, 1520, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23 (s, 1 H), 5.87–5.76 (m, 1 H), 5.63 (d, 0.5 H, J = 2.6 Hz), 5.57 (d, 0.5 H, J = 2.4 Hz), 4.34–4.14 (m, 4 H), 3.33 (s, 1.5 H), 3.28 (s, 1.5 H), 3.22 (s, 1.5 H), 3.21 (s, 1.5 H), 3.15–2.97 (m, 2 H), 1.31 (t, 3 H, J = 7.1 Hz), 1.30 (t, 3 H, J = 7.1 Hz), 0.15 (s, 4.5 H), 0.07 (s, 4.5 H). Anal. Calcd for $C_{18}H_{30}O_7Si$: C, 55.93; H, 7.82. Found: C, 55.74; H, 7.88.

Ethyl 1-[2-(ethoxycarbonyl)-2-methoxy-1-ethenyl]-2-methoxy-2-[(trimethylsilyl)oxy]cyclopent-3-ene-1-carboxylate (7) and 1-ethyl 8-methyl 4-(ethoxycarbonyl)-2-methoxyocta-2,6-diene-1,8-dioate (8): 1f (0.461 g, 2.0 mmol), (0.69 g, 4 mmol), acetate (0.0087 g, 0.02 mmol), (1:4); yield of **7**, 0.139 g (18%); IR (neat) 2990, 2900, 2840, 1720, 1640, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (s, 0.5 H), 6.68 (s, 0.5 H), 6.07 (m, 0.5 H), 5.98 (m, 0.5 H), 5.76 (m, 0.5 H), 5.62 (m, 0.5 H), 4.31–4.00 (m, 4 H), 3.70–3.20 (m, 1 H), 3.57 (s, 3 H), 3.30 (s, 1.5 H), 3.23 (s, 1.5 H), 2.28 (br d, 1 H, J = 19.6 Hz), 1.31–1.16 (m, 6 H), 0.13 (s, 4.5 H), 0.07 (s, 4.5 H). **7** was readily hydrolyzed on standing to the cyclopentenone, which could be characterized by elemental analysis. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.65; H, 6.48.

Yield of **8**: 0.314 g (50%); IR (neat) 2990, 2920, 2900, 2840, 1740 (sh), 1710, 1650, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.81 (dt, 1 H, J = 15.3, 7.2 Hz), 6.11 (d, 1 H, J = 9.8 Hz), 5.83 (d, 1 H, J = 15.3 Hz), 4.20 (q, 2 H, J = 7.2 Hz), 4.18 (m, superimposed, 1 H), 4.11 (q, 2 H, J = 7.1 Hz), 3.67 (s, 3 H), 3.65 (s, 3 H), 2.61 (dt, 1 H, J = 14.9, 7.2 Hz), 2.44 (dt, 1 H, J = 14.9, 7.2 Hz), 1.28 (t, 3 H, J = 7.1 Hz), 1.22 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 171.7, 166.2, 162.6, 147.5, 144.5, 123.1, 122.4, 61.0, 59.7, 51.2, 41.2, 34.3, 14.0. Anal. Calcd for $C_{15}H_{22}O_7$: C, 57.32; H, 7.05. Found: C, 57.40; H, 7.09.

2-Acetyl-6-methoxy-7-phenyl-6-[(trimethylsilyl)oxy]-cyclohepta-1,4-diene (4g): 1g (0.93 g, 5.0 mmol), (4.30 g, 25 mmol), pivalate (0.0313 g, 0.05 mmol), (1:6); yield, 1.17 g (71%) of a colorless gum; 1:1 mixture of diastereomers; IR (neat) 3060, 3020, 2940, 2900, 2820, 1715, 1650, 1600, 1490, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ one isomer 7.44–7.27 (m, 5 H), 7.00 (dd, 1 H, J = 6.5, 2.5 Hz), 5.94 (ddd, 1 H, J = 12.0, 7.9, 3.0 Hz), 5.71 (dd, 1 H, J = 12.0, 2.9 Hz), 4.14 (dd, 1 H, J = 6.5, 1.5 Hz), 3.55 (dd, 1 H, J = 19.2, 7.9 Hz), 3.28 (s, 3 H), 2.99 (br d, 1 H, J = 19.2 Hz), 2.32 (s, 3 H), –0.07 (s, 9 H); MS, m/z (relative intensity) 330 (42), 257

(33) Savard, J.; Brassad, P. *Tetrahedron* **1984**, *40*, 3455.

(27), 184 (53), 155 (27), 91 (25); HRMS calcd for $C_{19}H_{28}O_3Si$ 330.1651, found 330.1652.

Methyl 5-methyl-4-(2-phenyl-1-ethenyl)-2,3-dihydrofuran-2-acetate (9): **1g** (0.37 g, 2.0 mmol), (1.72 g, 10 mmol), acetate (0.009 g, 0.02 mmol), added over 2 h at 0 °C. The resulting solution was heated under reflux for 10 min and then cooled to room temperature. Citric acid (2.30 g, 12.0 mmol) in water (10 mL) was added, and the mixture was stirred for 20 min and then extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated. Purification by chromatography on alumina using diethyl ether–petroleum ether (1:19) gave **9** as a colorless gum: 0.179 g (35%); IR (neat) 3010, 2940, 2900, 2840, 1725, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.11 (m, 5 H), 6.88 (d, 1 H, J = 15.8 Hz), 6.08 (d, 1 H, J = 15.8 Hz), 4.98 (dq, 1 H, J = 10.5, 6.8 Hz), 3.72 (s, 3 H), 3.06 (br dd, 1 H, J = 13.3, 10.5 Hz), 2.79 (dd, 1 H, J = 15.7, 7.2 Hz), 2.56 (dd, 1 H, J = 15.7, 6.4 Hz), 2.51 (m, superimposed, 1 H), 1.95 (br s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 153.3, 138.2, 128.4, 126.2, 125.4, 123.6, 121.5, 109.1, 76.4, 51.7, 40.8, 35.8, 11.7; MS, m/z (relative intensity) 258 (100), 231 (10), 184 (62), 155 (36), 131 (73), 84 (39); HRMS calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1195.

1,1-Dimethylethyl 4-methoxy-4-[(trimethylsilyl)oxy]-cyclohepta-1,5-diene-1-carboxylate (4h): **1h** (0.84 g, 5.0 mmol), (1.72 g, 10 mmol), pivalate (0.031 g, 0.05 mmol), (3:17); yield, 1.09 g (74%) of a colorless gum; IR (neat) 2950, 1680, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (t, 1 H, J = 6.9 Hz), 5.80 (dt, 1 H, J = 11.8, 5.3 Hz), 5.65 (br d, 1 H, J = 11.8 Hz), 3.25 (s, 3 H), 3.15–3.11 (m, 2 H), 2.72 (d, 2 H, J = 6.9 Hz), 1.45 (s, 9 H), 0.14 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 166.3, 136.4, 136.0, 133.9, 128.6, 96.9, 80.5, 49.2, 38.7, 28.2, 26.2, 2.0. Anal. Calcd for $C_{16}H_{28}O_4Si$: C, 61.52; H, 9.03. Found: C, 61.51; H, 9.04.

Methyl 4-methoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (4i): **1i** (0.38 g, 3.0 mmol), (2.58 g, 15 mmol), pivalate (0.031 g, 0.05 mmol), (3:17); yield, 0.542 g (67%) of a colorless gum; IR (neat) 3020, 2950, 2900, 2820, 1710, 1650, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.97 (t, 1 H, J = 6.8 Hz), 5.81 (dt, 1 H, J = 11.8, 5.2 Hz), 5.67 (d, 1 H, J = 11.8 Hz), 3.71 (s, 3 H), 3.25 (s, 3 H), 3.18 (m, 2 H), 2.75 (d, 2 H, J = 6.8 Hz), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 167.3, 137.8, 137.7, 134.1, 133.9, 128.0, 96.7, 51.8, 49.1, 38.7, 26.2, 1.8; MS, m/z (relative intensity) 270 (21), 239 (27), 166 (33), 149 (33), 134 (46), 121 (40), 107 (53), 73 (100); HRMS calcd for $C_{13}H_{22}O_4Si$ 270.1287, found 270.1267.

Ethyl 3-ethenyl-4-methoxy-4-[(trimethylsilyl)oxy]cyclohepta-1,5-diene-1-carboxylate (4j): **1j** (0.58 g, 3.5 mmol), (3.45 g, 17.5 mmol), pivalate (0.0226 g, 0.035 mmol), (1:9); yield, 0.962 g (89%) of a colorless gum; IR (neat) 3070, 3010, 2960, 2900, 2820, 1700, 1660, 1440, 1400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96–6.88 (m, 1 H), 6.08–5.54 (m, 3 H), 5.17–5.04 (m, 2 H), 4.18 (q, 2 H, J = 7.1 Hz), 3.54 (m 1 H), 3.25 (s, 3 H), 3.19 (m, 2 H), 1.28 (t, 3 H, J = 7.1 Hz), 0.11 (s, 4.5 H), 0.09 (s, 4.5 H). Anal. Calcd for $C_{16}H_{26}O_4Si$: C, 61.90; H, 8.44. Found: C, 61.95; H, 8.46.

General Procedure for the Aqueous Citric Acid Hydrolysis of 4 to 10. A solution of **4** (0.74–1.79 mmol) and citric acid (2–3 equiv) in THF–H_2O (20–40 mL) was stirred for 1–1.5 h. The mixture was poured onto water and extracted with diethyl ether. The organic portion was washed with aqueous NaCl, dried ($MgSO_4$), and concentrated. The amounts of cycloheptadiene (**4a–c,g**), citric acid, and solvent used are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parentheses.

Diethyl 4-hydroxycyclohepta-1,3,5-triene-1,3-dicarboxylate (10a): **4a** (0.27 g, 0.74 mmol), (0.43 g, 2.20 mmol), (20 mL), (1:1); yield 0.19 g (100%) of a white solid, mp 43–47 °C; IR (Nujol) 2800 br, 1660, 1560, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.19 (s, 1 H), 7.61 (s, 1 H) 6.18–6.13 (m, 2 H), 4.35 (q, 2 H, J = 7.1 Hz), 4.23 (q, 2 H, J = 7.1 Hz), 2.77 (dd, 2 H, J = 4.6, 1.9 Hz), 1.38 (t, 3 H, J = 7.1 Hz), 1.31 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 173.1, 172.1, 166.1, 136.3, 131.3, 125.3, 119.9, 104.6, 61.6, 60.8, 26.0, 14.3, 14.2. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.88; H, 6.45.

Methyl 4-hydroxy-3-phenylcyclohepta-1,3,5-triene-1-carboxylate (10b): **4b** (0.43 g, 1.25 mmol), (0.73 g, 3.8 mmol), (30 mL), (1:1); yield, 0.292 g (97%) of an oil; IR (neat) 3550 br, 3000, 2980, 2930, 2860, 2820, 1660, 1620, 1510, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51–7.33 (m, 5 H), 7.30 (s, 1 H), 6.21 (d, 1 H, J = 10.0 Hz), 5.77 (dt, 1 H, J = 10.0, 6.8 Hz), 5.46 (s, 1 H), 3.74 (s, 3 H), 2.81 (d, 2 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 167.2, 155.8, 137.4, 136.4, 136.4, 129.6, 128.1, 127.4, 123.9, 120.1, 116.9, 52.1, 26.6; MS, m/z (relative intensity) 242 (35), 227 (20), 183 (100), 153 (15), 105 (15), 77 (12); HRMS calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0940.

Ethyl 4-hydroxy-3-(2-phenyl-1-ethenyl)cyclohepta-1,3,5-triene-1-carboxylate (10c): **4c** (0.692 g, 1.79 mmol), (1.03 g, 5.35 mmol), (20 mL), (1:1); yield, 0.491 g (97%) of a yellow oil; IR (neat) 3350 br, 3020, 2990, 2930, 1690, 1660, 1610, 1525, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60 (s, 1 H), 7.56 (d, 1 H, J = 16.0 Hz), 7.50 (m, 2 H), 7.40–7.13 (m, 3 H), 6.89, (s, 1 H), 6.70 (d, 1 H, J = 16.0 Hz), 6.17 (d, 1 H, J = 9.8 Hz), 5.85, (dt, 1 H, J = 9.8, 7.1 Hz), 4.29 (q, 2 H, J = 7.1 Hz), 2.75 (d, 2 H, J = 7.1 Hz), 1.35, (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 167.5, 156.2, 138.1, 133.5, 129.2, 129.1, 128.8, 127.5, 126.6, 124.4, 124.0, 119.3, 118.0, 61.5, 26.7, 14.6; MS, m/z (relative intensity) 282 (60), 253 (55), 209 (100), 194 (15), 179 (20), 165 (25), 131 (14), 115 (22), 91 (52), 77 (22); HRMS calcd for $C_{18}H_{18}O_3$ 282.1256, found 282.1252.

4-Acetyl-2-phenylcyclohepta-1,3,6-trien-1-ol (10g): **4g** (0.33 g, 1.0 mmol), (0.38 g, 2.0 mmol), (20 mL), (1:1); yield, 0.171 g (76%); IR (Nujol) 3320 br, 1700, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54–7.37 (m, 5 H), 7.11 (s, 1 H), 6.21 (d, 1 H, J = 9.9 Hz), 5.80 (dt, 1 H, J = 9.9, 7.1 Hz), 5.15 (br s, 1 H), 2.83 (d, 2 H, J = 7.1 Hz), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.5, 156.5, 137.6, 137.5, 137.5, 129.8, 128.9, 128.3, 127.4, 123.9, 120.1, 26.2, 25.1; MS, m/z (relative intensity) 261 (5), 226 (15), 183 (100), 161 (10), 122 (10), 105 (20), 77 (20); HRMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0996.

Ethyl 4-Hydroxy-1-(phenylsulfonyl)cyclohepta-1,3,5-triene-3-carboxylate (10e). A mixture of **4e** (0.561 g, 1.32 mmol) and 20% HCl (10 mL) was stirred in THF (10 mL) for 1 h. The mixture was poured onto water and extracted with diethyl ether. The organic portion was washed with aqueous NaCl, dried ($MgSO_4$), and concentrated. Chromatography on silica using diethyl ether–petroleum ether (1:1) afforded pure **10e** as a colorless oily solid: 0.315 g (75%); IR (Nujol) 1640, 1610, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.30 (s, 1 H), 7.90–7.88 (m, 2 H), 7.70 (s, 1 H), 7.60–7.51 (m, 3 H), 6.13 (d, 1 H, J = 10.3 Hz), 5.87 (dt, 1 H, J = 10.3, 7.1 Hz), 4.36 (q, 2 H, J = 7.1 Hz), 2.70 (d, 2 H, J = 7.1 Hz), 1.38 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 173.2, 171.4, 140.3, 135.2, 133.0, 130.4, 129.0, 128.6, 127.7, 126.0, 102.7, 61.8, 25.6, 14.1; MS, m/z (relative intensity) 320 (5), 274 (9), 179 (70), 133 (100), 105 (10), 77 (17); HRMS calcd for $C_{16}H_{16}O_5S$ 320.0718, found 320.0712.

General Procedure for the DDQ Oxidation of 10 to 5. A mixture of **10** (1 equiv) and DDQ (1.2–2 equiv) was heated at reflux in benzene (20 mL) for 12–24 h. The solution was filtered, the residual solid material was washed with benzene, and the combined solutions were concentrated. The amounts of cycloheptadiene (**10a–c,e,g**), DDQ, and solvent used, as well as reaction time, are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parentheses.

2,4-Bis(ethoxycarbonyl)cyclohepta-2,4,6-trien-1-one (5a): **10a** (0.33 g, 1.3 mmol), (0.59 g, 2.64 mmol), (20 mL), 12 h, (3:1); yield, 0.302 g (92%) of an oily red solid; IR 2980, 1700, 1640, 1580, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22 (d, 1 H, J = 1.5 Hz), 8.00 (ddd, 1 H, J = 6.2, 3.3, 1.5 Hz), 7.23–7.18 (m, 2 H), 4.37 (q, 2 H, J = 7.1 Hz), 4.36 (q, 2 H, J = 7.1 Hz), 1.38 (t, 3 H, J = 7.1 Hz), 1.37 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 183.8, 166.7, 165.1, 145.4, 142.3, 139.4, 134.1, 134.0, 133.5, 62.6, 62.0, 14.1, 14.0; MS m/z (relative intensity) 250 (50), 221 (25), 205 (100), 194 (25), 177 (100), 166 (40), 149 (70), 121 (30), 76 (100); HRMS calcd for $C_{13}H_{14}O_5$ 250.0841, found 250.0836. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.35; H, 5.64. Found: C, 62.31; H, 5.67.

4-(Methoxycarbonyl)-2-phenylcyclohepta-2,4,6-trien-1-one (5b): **10b** (0.12 g, 0.50 mmol), (0.23 g, 1.0 mmol), (25 mL), 24 h, (1:1); yield, 0.117 g (98%) of a red solid, mp 102–104 °C; IR (KBr) 1710, 1630, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07 (d, 1 H, J = 1.5 Hz), 7.92 (ddd, 1 H, J = 6.2, 2.8, 1.5 Hz), 7.54–7.49 (m, 2 H), 7.42–7.38 (m, 3 H), 7.25–7.21 (m, 2 H), 3.92 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.2, 166.8, 151.6, 145.2, 139.7, 136.3, 134.5, 134.4, 133.7, 129.4, 128.9, 128.4, 53.4. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.04. Found: C, 74.93; H, 5.10.

4-(Ethoxycarbonyl)-2-(2-phenyl-1-ethenyl)cyclohepta-2,4,6-trien-1-one (5c): **10c** (0.349 g, 1.44 mmol), (0.39 g, 1.72 mmol), (20 mL), stirred at room temperature for 12 h, (1:1); yield, 0.090 g (22%) of a yellow oil; IR (neat) 3020, 2960, 2920, 2810, 1710, 1620, 1585, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.34 (d, 1 H, J = 1.1 Hz), 7.91 (ddd, 1 H, J = 5.8, 3.8, 1.1 Hz), 7.60–7.20 (m, 9 H), 4.31 (q, 2 H, J = 7.1 Hz), 1.31 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 185.6, 166.4, 147.4, 143.0, 136.8, 135.3, 135.2, 134.5, 133.7, 130.2, 128.8, 128.7, 127.5, 126.4, 62.4, 14.2; MS, m/z (relative intensity) 280 (45), 251 (29), 207 (20), 178 (24), 148 (13), 111 (19), 91 (100), 71 (35); HRMS calcd for $C_{18}H_{16}O_3$ 280.1099, found 280.1073.

2-(Ethoxycarbonyl)-4-(phenylsulfonyl)cyclohepta-2,4,6-trien-1-one (5e): **10e** (0.315 g, 0.98 mmol), (0.45 g, 1.97 mmol), (20 mL), 12 h, (1:1); yield, 0.204 g (65%) of a red oil; IR (neat) 2990, 1710, 1620, 1590, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04 (br d, 1 H, J = 7.7 Hz), 7.93–7.86 (m, 3 H), 7.69–7.51 (m, 3 H), 7.24 (dd, 1 H, J = 11.7, 7.7 Hz), 7.12 (dd, 1 H, J = 11.7, 1.3 Hz), 4.31 (q, 2 H, J = 7.1 Hz), 1.31 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 183.1, 165.4, 145.6, 145.2, 142.4, 138.8, 137.3, 134.4, 132.3, 131.0, 129.8, 128.1, 62.4, 14.0; MS, m/z (relative intensity) 318 (17), 262 (35), 245 (95), 218 (15), 197 (35), 149 (19), 125 (100), 105 (60), 77 (80); HRMS calcd for $C_{16}H_{14}O_5S$ 318.0562, found 318.0549.

4-Acetyl-2-phenylcyclohepta-2,4,6-trien-1-one (5g): **10g** (0.15 g, 0.68 mmol), (0.18 g, 0.80 mmol), (25 mL), 12 h, (1:1); yield, 0.105 g (69%) of an orange solid, mp 94–95 °C; IR (Nujol) 1680, 1620, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (d, 1 H, J = 1.5 Hz), 7.66 (ddd, 1 H, J = 4.7, 4.7, 1.5 Hz), 7.55–7.32 (m, 5 H), 7.30–7.10 (m, 2 H), 2.58 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.7, 186.1, 151.4, 111.6, 141.0, 139.6, 135.1, 133.7, 133.0, 129.2, 128.7, 128.2, 26.5. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.26; H, 5.44.

4-(Ethoxycarbonyl)-2-(phenylsulfonyl)cyclohepta-2,4,6-trien-1-one (5d). A mixture of **4d** (0.545 g, 1.28 mmol) and 20% HCl (10 mL) was stirred in THF (10 mL) for 2 h. The mixture was poured onto water and extracted with diethyl ether. The organic portion was washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. **10d** was characterized spectroscopically: IR (neat) 3160, br, 3060, 2980, 2930, 2900, 1690, 1620, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.01 (s, 1 H), 7.87 (m, 2 H), 7.65–7.50 (m, 3 H), 7.38 (s, 1 H), 6.15 (d, 1 H, J = 10.0 Hz), 6.04 (dt, 1 H, J = 10.0, 6.7 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 2.66 (d, 2 H, J = 6.7 Hz), 1.27 (t, 3 H, J = 7.1 Hz); MS, m/z (relative intensity) 320 (8), 291 (9), 247 (37), 178 (20), 147 (45), 122 (27), 105 (100), 77 (76); HRMS calcd for $C_{16}H_{16}O_5S$ 320.0718, found 320.0711. Crude **10d** from above, DDQ (0.58 g, 2.56 mmol), and *p*-toluenesulfonic acid (0.1 g) were stirred in benzene (20 mL) for 12 h at room temperature. The mixture was filtered, the solid material was washed with benzene, and the combined organic solutions were then concentrated. Purification by chromatography on silica using diethyl ether–ethyl acetate (1:1) afforded pure **5d** as a red solid: 0.311 g (76%); IR (neat) 3040, 2980, 2920, 1700, 1620, 1590, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.16 (d, 1 H, J = 1.4 Hz), 8.13 (d, 1 H, J = 8.4 Hz), 8.06–8.01 (m, 2 H), 7.63–7.45 (m, 3 H), 7.25 (dd, 1 H, J = 12.1, 8.4 Hz), 7.09 (d, 1 H, J = 12.1 Hz), 4.42 (q, 2 H, J = 7.1 Hz), 1.40 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 180.5, 164.6, 148.6, 147.0, 142.0, 139.5, 137.8, 134.2, 133.7, 133.3, 129.3, 128.7, 63.1, 14.2. Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.37; H, 4.43. Found: C, 60.48; H, 4.45.

4-[(1,1-Dimethylethoxy)carbonyl]cyclohepta-2,4,6-trien-1-one (5h). A mixture of **4h** (0.30 g, 1.0 mmol) and citric acid (0.58 g, 3.0 mmol) was stirred in THF (10 mL) and water (10 mL) for 1.5 h. The mixture was poured onto water and extracted with diethyl ether. The organic portion was washed with aqueous NaCl, dried ($MgSO_4$), and then concentrated. The crude material, DDQ (0.34 g, 1.5 mmol), and *p*-toluenesulfonic acid (0.015 g) were heated at reflux in benzene (20 mL) for 3 h. The mixture was filtered, the solid material was washed with benzene, and the combined organic solutions were then concentrated. Purification by chromatography on silica using diethyl ether–petroleum ether (3:1) afforded pure **5h** as a red solid: 0.096 g (47%), mp 44–46 °C; IR 2960, 2900, 1700, 1620, 1575, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79 (br d, 1 H, J = 7.8 Hz), 7.71 (br d, 1 H, J = 12.4 Hz), 7.25–6.94 (m, 3 H), 1.51 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 187.5, 164.5, 144.9, 140.8, 137.3, 137.1, 134.8, 134.6, 82.9, 27.9; MS, m/z (relative intensity) 206 (40), 151 (70), 133 (30), 122 (30), 105 (50), 77 (40); HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0940.

5h was also formed by heating at reflux a mixture of **4h** (0.30 g, 1.0 mmol) and $VO(OEt)Cl_2$ (0.37 g, 2.0 mmol) in ethanol for 0.5 h. Concd HCl (4 drops) was then added, and the mixture was poured onto saturated NaCl solution and extracted twice with diethyl ether. The extracts were dried ($MgSO_4$) and then concentrated. Purification by chromatography on silica using ether–petroleum ether (7:13) afforded **5h** (0.097 g, 47%).

4-(Methoxycarbonyl)-2-phenylcyclohepta-2,4,6-trien-1-one (5b). A mixture of **4b** (0.39 g, 1.0 mmol) and $VO(OEt)Cl_2$ (0.37 g, 2.0 mmol) was heated at reflux in ethanol for 0.5 h. Concd HCl (4 drops) was then added, and the mixture was poured onto a saturated NaCl solution and extracted twice with diethyl ether. The extracts were dried ($MgSO_4$) and then concentrated. Purification by chromatography on silica using ether–petroleum ether (1:1) afforded **5b** (0.171 g, 71%).

4-(Methoxycarbonyl)cyclohepta-2,4,6-trien-1-one (5i). A mixture of **4i** (0.425 g, 1.57 mmol) and $VO(OEt)Cl_2$ (1.02 g, 5.5 mmol) was heated at reflux in ethanol for 0.5 h. Concd HCl (4 drops) was then added, and the mixture was poured onto a saturated NaCl solution and extracted twice with diethyl ether. The extracts were dried ($MgSO_4$) and then concentrated. Purification by chromatography on silica using ether–petroleum ether (1:4) afforded **5i**, which was spectroscopically identical with the previously reported data.[24b]

4-(Ethoxycarbonyl)-2-(2-phenylethyl)cyclohepta-2,4,6-trien-1-one (12c). A sample of **4c** (0.390 g, 1.03 mmol) was stirred with HCl gas in THF (25 mL) for 24 h. The mixture was poured onto water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Purification by chromatography on silica using diethyl ether–petroleum ether (1:4) afforded pure product as a yellow oil: 0.123 g (42%); IR (neat) 3030, 3010, 2990, 2920, 2860, 1710, 1630, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86–7.83 (m, 2 H), 7.31–7.11 (m, 7 H), 4.34 (q, 2 H, J = 7.1 Hz), 3.04–2.83 (m, 4 H), 1.37 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 186.4, 166.2, 153.8, 143.4, 141.3, 135.6, 134.5, 133.7, 133.2, 128.6, 128.3, 126.0, 62.3, 38.2, 34.9, 14.2; MS, m/z (relative intensity) 282 (55), 253 (20), 209 (19), 177 (10), 149 (6), 123 (5), 91 (100); HRMS calcd for $C_{18}H_{18}O_3$ 282.1256, found 282.1262.

4-(Ethoxycarbonyl)-2-ethylcyclohepta-2,4,6-trien-1-one (12j). A mixture of **4j** (0.318 g, 1.0 mmol) and citric acid (0.58 g, 3.0 mmol) in THF (10 mL) and water (10 mL) was stirred for 1 h. The mixture was poured onto water and extracted with diethyl ether. The organic phase was dried ($MgSO_4$) and then concentrated. The mixture was dissolved in THF (20 mL), and HCl gas was bubbled through for 20 min. The mixture was poured onto water, neutralized with NaOH, and extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and then concentrated. Purification by chromatography on silica using ethyl acetate–petroleum ether (1:19 to 3:17) afforded pure product as a yellow oil: 0.082 g, (39%); IR (neat) 2990, 2840, 2780, 1715, 1620, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (br s, 1 H), 7.84 (m, 1 H), 7.25–7.07 (m, 2 H), 4.36 (q, 2 H, J = 7.1 Hz), 2.70 (q, 2 H, J = 7.4 Hz), 1.38 (t, 3 H, J = 7.1 Hz), 1.19 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 186.4, 166.4, 156.4, 143.1, 135.2, 134.6, 133.6, 131.8, 62.2, 28.8, 14.2, 13.2; MS, m/z (relative intensity) 206 (65), 177 (10), 163 (6), 133 (100), 105 (40), 91 (10), 77 (30); HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0948. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.98; H, 6.88.

Nezukone (15). Methyllithium (2.0 mL, 1.6 M, 2.8 mmol) in diethyl ether was added to a solution of **4h** (0.285 g, 1.0 mmol) in THF (10 mL) at −78 °C. The mixture was allowed to warm to room temperature over a 2-h period, then cooled once again to −78 °C, and quenched with water. The mixture was extracted with diethyl ether, and the organic layer was then dried (Na_2SO_4) and concentrated. The crude material was stirred for 0.5 h with concd HCl (2 mL) in THF (4 mL), diluted with water, and then extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and concentrated. Purification by chromatography on silica using ethyl acetate–petroleum ether (3:7 to 6:4) afforded **15**: 0.093 g (59%); IR (neat) 3020, 2960, 2920, 2860, 1700, 1625, 1565, 1520, 1450 cm^{-1}; ^1H NMR (C_6D_6) δ 7.01–6.87 (m, 2 H), 6.36–6.26 (m, 2 H), 6.07 (br d, 1 H, J = 8.6 Hz), 2.07 (septet, 1 H, J = 6.8 Hz), 0.77 (d, 6 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 187.9, 156.0, 141.7, 139.9, 137.9, 137.0, 130.3, 37.9, 22.8; MS, m/z (relative intensity) 148 (25), 120 (5), 105 (100), 91 (7), 77 (18); HRMS calcd for

$C_{10}H_{12}O$ 148.0888, found 148.0884. The spectral data for **15** was consistent with the reported data.[21f]

Acknowledgment. We thank Ms. Mary Uhrig from R. J. Reynolds Tobacco Company for the mass spectral determinations. Financial support of this work by the National Science Foundation (CHE 8517881) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. **1a**, 104525-94-2; **1b**, 119987-21-2; **1c**, 126554-34-5; **1d**, 126554-33-4; **1e**, 134418-82-9; **1f**, 126554-43-6; **1g**, 134418-83-0; **1h**, 132524-91-5; **1i**, 126554-35-6; **1j**, 132524-92-6; **2** (isomer 1), 110362-29-3; **2** (isomer 2), 110362-30-6; **4a** (isomer 1), 136175-46-7; **4a** (isomer 2), 136175-47-8; **4b** (isomer 1), 136175-48-9; **4b** (isomer 2), 136175-49-0; **4c** (isomer 1), 136175-50-3; **4c** (isomer 2), 136175-51-4; **4d** (isomer 1), 136175-52-5; **4d** (isomer 2), 136175-53-6; **4e** (isomer 1), 136175-54-7; **4e** (isomer 2), 136175-55-8; **4f** (isomer 1), 136175-56-9; **4f** (isomer 2), 136175-57-0; **4g** (isomer 1), 136175-58-1; **4g** (isomer 2), 136175-59-2; **4h**, 136175-60-5; **4i**, 136175-61-6; **4j**, 136175-62-7; **5a**, 136175-63-8; **5b**, 136175-64-9; **5c**, 136175-65-0; **5d**, 136175-66-1; **5e**, 136175-67-2; **5f**, 136175-63-8; **5g**, 136175-68-3; **5h**, 136175-69-4; **5i**, 108462-35-7; **6** (isomer 1), 136175-70-7; **6** (isomer 2), 136235-12-6; **7**, 136175-71-8; **8**, 136175-72-9; **9**, 136175-73-0; **10a**, 136175-74-1; **10b**, 136175-75-2; **10c**, 136175-76-3; **10e**, 136175-77-4; **10g**, 136175-78-5; **12c**, 136175-79-6; **12j**, 136175-80-9; **15**, 13656-81-0; $Rh_2(OAc)_4$, 15956-28-2; $Rh_2(Piv)_4$, 65545-21-3.

Supplementary Material Available: Copies of the ^1H NMR spectra for compounds **4d**, **4g**, **4i**, **5c**, **5e**, **5h**, **9**, **10b**, **10c**, **10e**, **10g**, and **12b** (12 pages). Ordering information is given on any current masthead page.

New Low-Valent Titanium Reagents for Dicarbonyl Coupling and Their Use in a General Method of Annulation

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Received May 20, 1991

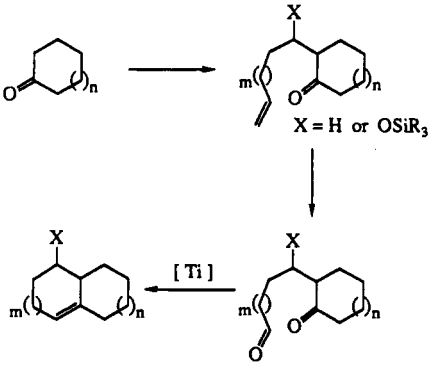
New low-valent titanium reagents have been prepared by reducing $TiCl_3$ (1 mol) with C_8K (2 mol) or by reducing $TiCl_4$ (1 mol) with Na–naphthalene (2.75 mol). Ketones carrying a chain that incorporates a suitably placed oxo function (aldehyde or ketone) undergo intramolecular dicarbonyl coupling to produce a bicyclic compound when treated with an excess (16–17 mol of titanium halide per mol of dicarbonyl compound) of one of these reagents. The procedure works well even for highly oxygenated substrates and constitutes a general method of annulation. Other reducing agents besides C_8K or Na–naphthalene are suitable, and a brief examination of Na(Hg) and Na–K alloy was made. The $C_8K/TiCl_3$ system was also used to convert a *cis*-1,2-diol into the corresponding olefin.

We report here full details of the development of some new low-valent titanium reagents in which the metal has formally a valency of 1. These reagents can be used in a general method of annulation (see Scheme I)[1] and, unlike some other low-valent titanium species that we have tested, also work with highly oxygenated compounds.

Introduction

The McMurry reaction,[2] in which carbonyl compounds—usually ketones or aldehydes—are coupled by use of low-valent titanium to produce olefins, has served for many years as an extremely useful procedure.[3] The reagent is tentatively regarded[4,5] as a titanium(0) species, and the scope of the method has been examined in detail.[3a] The reaction is heterogeneous, and so the mechanism is a difficult one to probe, although considerable progress has been made.[3a,4]

Scheme I



Several years ago, as a model study[6] for the synthesis[7] of compactin and mevinolin, we treated compounds **1** under standard conditions[8] with the titanium reagent

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