for **29** and **30** in 85.1% yield as colorless needles: mp 211–212 °C (ethyl acetate–hexane); IR 3300 (OH), 1720 (C=O), 1670 (C=CC=O) cm^{-1}; 400-MHz NMR δ 0.89 (3 H, s, 13-Me), 0.94 (3 H, d, J = 6.6 Hz, 24-Me), 0.96 (3 H, s, 10-Me), 1.17 (3 H, s, 25-CMe), 1.21 (3 H, s, 25-CMe), 1.28 (3 H, s, 20-Me), 2.04 and 2.12 (6 H, each s, 2 × $MeCO_2$), 4.66–4.76 (1 H, m, 3-H), 4.97 (1 H, distorted d, J = 5.5 Hz, 22-H), 5.87 (1 H, s, 7-H); MS, m/z 562 (M^+); exact mass calcd for $C_{32}H_{48}O_7$ ($M^+ - H_2O$) 544.3400, found 544.3408.

Acknowledgment. We thank Prof. D. H. S. Horn for providing the natural 2-deoxycrustecdysone. We also thank Ms. T. Ogata, T. Tanaka, M. Yuyama, H. Kasai, and M. Moriki of Hoshi University for microanalysis, spectral measurements, and manuscript preparation. Financial support from the Ministry of Education, Science, and Culture and The Sendai Institute of Heterocyclic Chemistry is deeply acknowledged.

Regioselective Preparation of Vinylcyclopentadienes and Selected Cycloadditions

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Received October 16, 1985

A variety of vinylcyclopentadienes have been prepared by deprotonation of fulvenes with LDA at −78 °C and quenching with acid at 0 °C. The compounds were present as a mixture of valence tautomers, the 1-substituted isomer dominating over the 2-substituted isomer by a ratio of 2:1. In all instances the regioisomer with the 1,1-disubstituted ethylene side chain was formed. No isomer with a trisubstituted exocyclic double bond was discernible by NMR. Fulvenes are thermodynamically more stable than the less highly substituted vinylcyclopentadienes. Thus, on contact with base vinylcyclopentadienes rearrange to fulvenes. Vinylcyclopentadienes react with acetylenedicarboxylic acid dimethyl ester to give Diels–Alder adducts, e.g., **7a** and also bis adduct **8a**. Intramolecular Diels–Alder reactions of appropriately substituted vinylcyclopentadienes are feasible in a protic solvent such as 1,2-ethanediol on heating to 190 °C. In this case, the isomerization of the substituted vinylcyclopentadiene to substituted fulvene is a side reaction only.

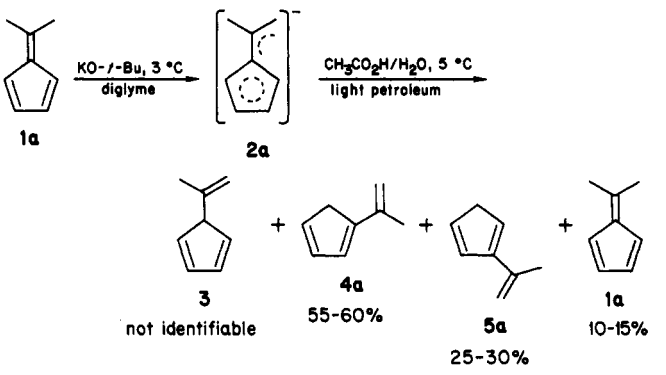
Vinylcyclopentadienes can be regarded as isomers or tautomers of fulvenes. Although fulvenes have considerable synthetic potential and have been studied in great detail,[1] very little is known about vinylcyclopentadienes. Several years ago Hine and Knight[2] reported the KO-*t*-Bu-induced deprotonation of the simple 6,6-dimethylfulvene (**1a**) and after quenching with aqueous acetic acid at 5 °C obtained the three isomeric trienes **4a**, **5a**, and **1a**, a typical product composition being shown in Scheme I. The results obtained and the product distribution were discussed in terms of the principle of least nuclear motion.[3] More recently, Rausch et al.[4] have deprotonated **1a** and trapped the resulting anion as η^5 organometal complex, e.g., **2a** → **6** (Scheme II). Polymers of type **6** are useful for a variety of applications.

In context with a number of mechanistic and preparative studies we required a flexible and efficient synthesis of vinylcyclopentadienes. It was especially important to generate the substituted vinylic double bond regioselectively so that the number of potential tautomers would be minimized.

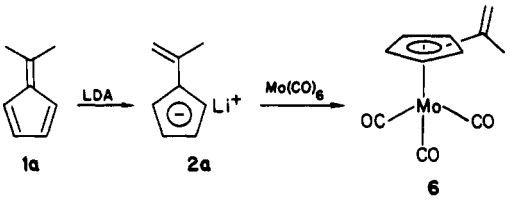
Results

As a model we decided to reinvestigate 6,6-dimethylfulvene (**1a**), confirming the work of Hine and Knight.[2] In our hands deprotonation of **1a** with LDA/THF at −78 °C followed by quenching with aqueous acid at 0 °C typically

Scheme I



Scheme II



gave **4a** (60%), **5a** (30%), and **1a** (10%) in 80% yield (with respect to **1a** used). **4a** and **5a** can be identified and distinguished by NMR. The signals of the vinylic methylene protons are characteristic. At 90 MHz the major isomer **4a** shows two broad singlets at 4.77 and 5.07 ppm, i.e., separated by 26 Hz. The minor isomer **5a** shows two broad singlets at 4.96 and 5.20 ppm, separated by 22 Hz. This pattern was observed for other vinylcyclopentadienes, e.g., **4b** and **5b**, **13c**α and **13c**β, and **13d**α and **13d**β. We have also identified the two pairs of valence isomers **4a**/**5a** and **4b**/**5b** by Diels–Alder addition with acetylenedicarboxylic acid dimethyl ester (Scheme III).

(1) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41. Hafner, K.; et al. *Angew. Chem.* **1963**, *75*, 35. Houk, K. N.; Luskus, L. J. *Tetrahedron Lett.* **1970**, 4029. Brown, E. D.; Clarkson, R.; Leeney, T. J.; Robinson, G. E. *J. Chem. Soc. Chem. Commun.* **1974**, 642. Gupta, I.; Yates, P. *Synth. Commun.* **1982**, *12*, 1007. Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.
(2) Hine, J.; Knight, D. B. *J. Org. Chem.* **1970**, *35*, 3949. Knight, D. B.; Hartless, R. L.; Jarvis, D. A. *J. Org. Chem.* **1972**, *37*, 688.
(3) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 51.
(4) Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Priester, R. D.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 884.

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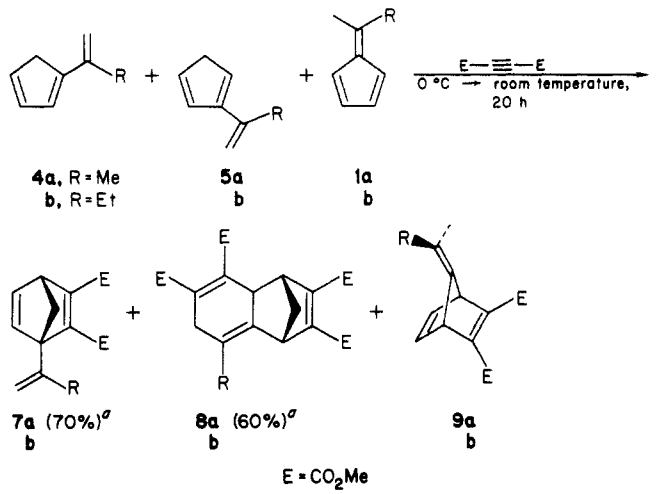
Scheme III[a]



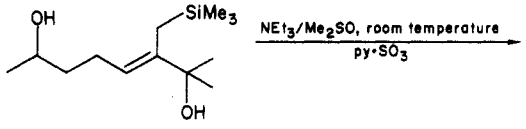
[a] The yields refer to the amount of valence isomer in the mixture of valence isomers.

As one can see the 2-vinyl-substituted valence isomers **5a** and **5b** cannot be trapped with the dienophile as the monoadduct but rather as the bis adducts **8a** and **8b**. Fortunately, this fact facilitates the separation and isolation of products.

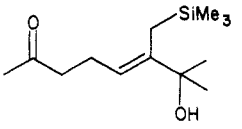
The deprotonation of 6-ethyl-6-methylfulvene (**1b**) was a first test for the regioselectivity of the reaction and the formation of regioisomeric vinylcyclopentadienes. Since it is well established that deprotonation of ketones with LDA/THF at −78 °C gives the less substituted, kinetic enolate, we deprotonated **1b** under similar conditions. We were pleased to find that the vinylcyclopentadiene isomer having a terminal methylene bond was formed. The regioisomers resulting from protonation of anion **2c** were not detected by ^{1}H NMR (Scheme IV).

Functionalized Vinylcyclopentadienes via Functionalized Fulvenes. The required fulvenes **11a–e** were prepared by the base-catalyzed aldol-like condensation of cyclopentadiene and ketones **10a–e** (Chart I). Ketones **10c** and **10d** were prepared via fragmentation of the corresponding epoxy ketones.[5] Oxidation of the acid labile alcohol **12** to **10e** was tried unsuccessfully with pyridinium dichlorochromate (PDC) and by Swern oxidation.[6]

However, oxidation with SO_3–pyridine as described by Parikh and Doering[7] was satisfactory.



12



10e (50%)

The yields of fulvenes were in the range of 50–60%; only in the instance of the sterically hindered ketone **10d** was the yield of **11d** poor. Using the classical method of Thiele, i.e., NaOEt/EtOH as base we obtained practically no fulvene **11d**. Preformed sodium cyclopentadienide and THF solvent[8] gave **11d** in 15% yield. For the preparation of **11e** best results were obtained with a suspension of cyclopentadienyllithium in THF.[9] Presumably, the reactivity of the cyclopentadienyl anion is moderated in this fashion and fewer side reactions ensue[10] (Chart II).

Following the model studies on fulvenes **1a** and **1b** we deprotonated the functionalized fulvenes **11a–e** with LDA at −78 °C. In the case of fulvenes **11c–e** we assume that dianions are formed as intermediates. Evidence for a dianion is the increased amount of solvent THF necessary to maintain a homogeneous solution. Thus, isomerization of fulvene **11c** required a twofold quantity of THF compared with fulvene **11a**. As in the model work the car-

Scheme IV

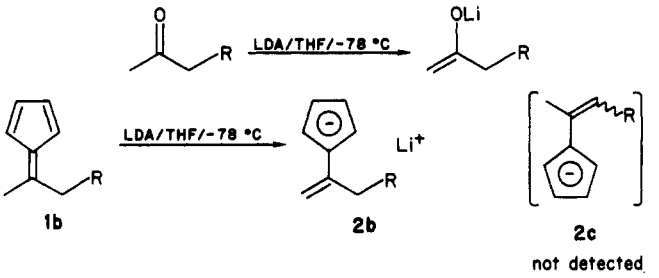
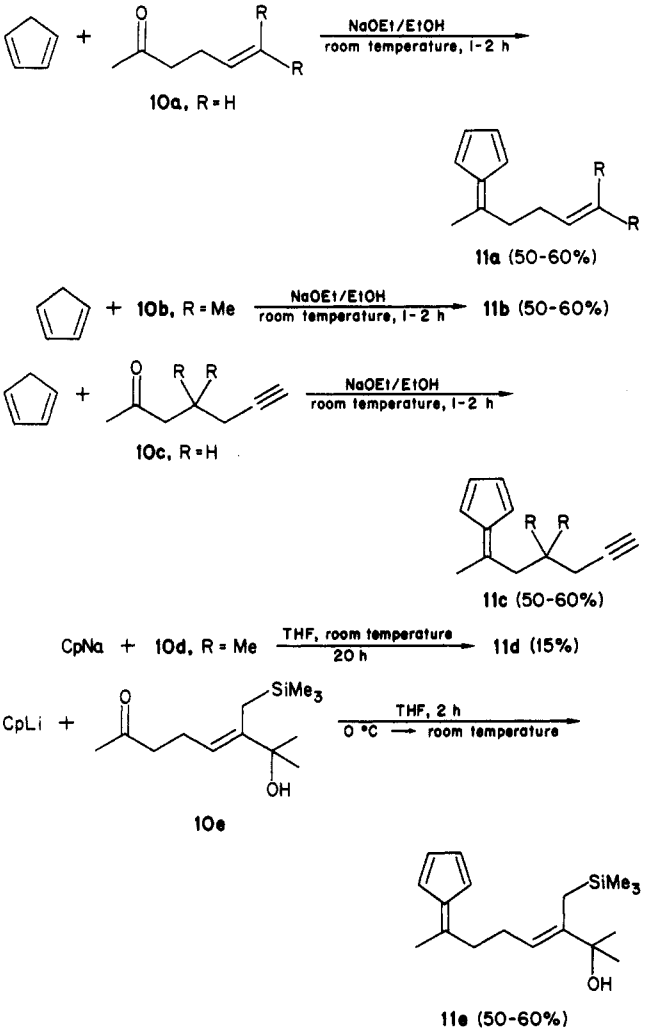
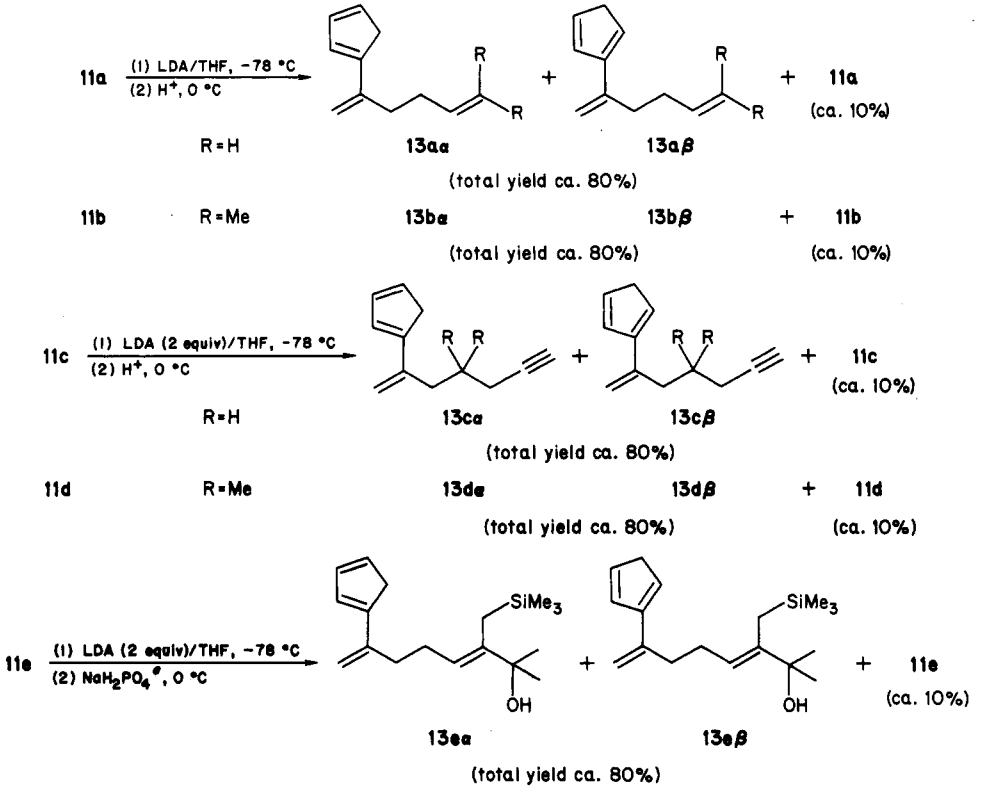


Chart I. Functionalized Fulvenes Prepared. Survey



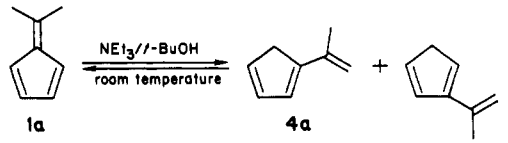
(5) Felix, D.; Schreiber, J.; Ohloff, G.; Eschenmoser, A. *Helv. Chim. Acta* **1971**, *54*, 2896.
(6) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.
(7) Parikh, J. R.; Doering, W. von E. *J. Am. Chem. Soc.* **1967**, *89*, 5505.
(8) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F. *J. Org. Chem.* **1984**, *49*, 201.
(9) Knight, D. B.; Hall, R. W.; Cleary, D. G. *J. Heterocycl. Chem.* **1981**, *18*, 1649.
(10) Neuenschwander, M.; Schädeli, U. *Chimia* **1981**, *35*, 476.

Chart II. Regioselective Isomerization to Vinylcyclopentadienes



[a] Quenching with NaH_2PO_4 buffer instead of 1 N HCl was essential because of the acid labile side chain.

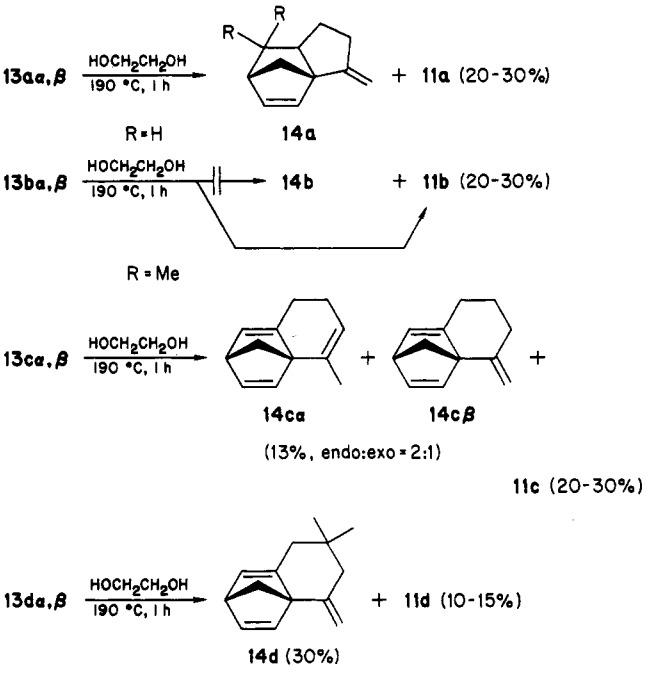
banionic solution was quenched carefully, by being syringed into an excess of aqueous hydrochloric acid which was vigorously stirred and maintained at 0 °C. The mixture of isomers was analyzed by GC and NMR. Interestingly, the resulting vinylcyclopentadienes were again formed regioselectively, in analogy to the formation of **4b** and **5b** from **1b**. 1-Substituted vinylcyclopentadienes (α series) and the 2-substituted vinylcyclopentadienes (β series) were formed in the ratio of 2:1. In all cases the corresponding fulvenes **11a–e** were isolated in ca. 10% yield. An equilibration experiment showed that fulvenes are thermodynamically more stable than the valence isomeric vinylcyclopentadienes **4a** + **5a**. Because of the



facile Diels–Alder dimerization of **4a** and **5a** a precise determination of the equilibrium is not straightforward, but we estimate that less than 10% of **4a** + **5a** are in equilibrium with **1a**. We assume that the homologues of **1a** behave similarly (Chart III).

An attempted intramolecular cycloaddition of **13bα,β** was not successful. Instead, the more stable fulvene valence isomer **11b** was observed. However, a more reactive 2π component (**13aα,β** → **14a**) and the geminal dimethyl effect (**13dα,β** → **14d**) were helpful for tricyclization. Apparently, the greater the amount of tricyclic product, the less fulvene formed. It is interesting that the isomerization to fulvene at 190 °C in 1,2-ethanediol is still relatively slow, whereas it is rapid at room temperature in the presence of *base* (pK_a of cyclopentadiene ca. 16). It is noticeable that tricyclization of **13cα,β** gives two

Chart III. Intramolecular Diels–Alder Reactions of Vinylcyclopentadienes

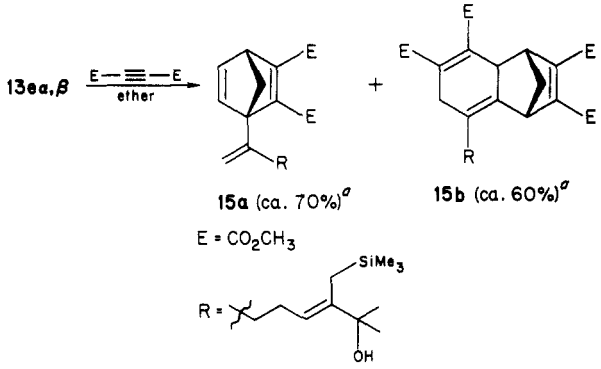


isomeric adducts **14cα** and **14cβ**. The primary adduct **14cβ** undergoes isomerization to the more stable endocyclic isomer **14cα** under the reaction conditions (**14cα**:**14cβ** = 2:1). Interestingly, the corresponding isomerization can be stopped in the geminal dimethyl homologue **14d**. No endocyclic isomer was detectable in this instance.

In context with approaches to zizaene[11] the preparation of **13eα** and **13eβ** was of interest. Since these two isomeric vinylcyclopentadienes were sensitive they were identified

(11) Hoffmann, H. M. R.; Henning, R. *Helv. Chim. Acta* **1983**, *66*, 828.

Scheme V



by intermolecular Diels–Alder addition with acetylenedicarboxylic acid dimethyl ester (Scheme V).

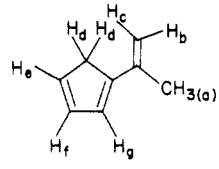
Conclusions

A variety of vinylcyclopentadienes have been prepared from the corresponding fulvenes in good yield (ca. 70%). The resulting vinylcyclopentadienes are formed regioselectively under our conditions, i.e., the vinylic double bond is 1,1-disubstituted and not trisubstituted. On contact with base vinylcyclopentadienes rearrange to the thermodynamically more stable fulvenes. However, in a protic solvent such as 1,2-ethanediol intramolecular Diels–Alder reactions of vinylcyclopentadienes are feasible, even at 190 °C, with formation of exo-methylene-substituted tricyclo[5.2.1.0^{1,5}]dec-8-ene system **14a** and tricyclo[6.2.1.0^{1,6}]-undeca-6,9-dienes **14c,d**.

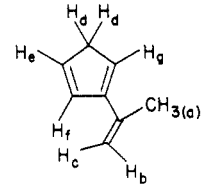
Experimental Section

1- and 2-(1-Methylethenyl)-1,3-cyclopentadiene (4a, 5a). 5-(1-Methylethylidene)-1,3-cyclopentadiene (6,6-dimethylfulvene) (**1a**) was prepared by the standard method.[12] A 1.6 M solution (12.5 mL) of *n*-butyllithium (20 mmol) in hexane was dropped under N_2 to a solution of diisopropylamine (2.8 ml, 20 mmol) in absolute THF (30 mL) at −78 °C. The solution was allowed to reach room temperature and then recooled to −78 °C. **1a** (2.1 g, 19.8 mmol) in absolute THF (10 mL) was added dropwise. After being warmed to ca. 0 °C, the reaction solution was syringed under vigorous stirring into a mixture of 1 N hydrochloric acid (200 mL) and ice (400 mL). The aqueous phase was extracted with pentane (3 × 100 mL), the combined organic phase was washed with water (2 × 100 mL) and dried ($MgSO_4$), and the solvent was removed at 0 °C → room temperature in vacuo to leave ca. 5 mL (ca. 80%) of a light yellow oil which was used for the various reactions (see below).

The 90-MHz ^{1}H NMR ($CDCl_3$, ppm) data of **4a** and **5a** are as follows:



4a



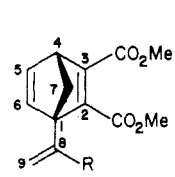
5a

	H_a	H_b	H_c	H_d	H_e	H_f	H_g
4a	1.95	4.77	5.07	3.11	~6.27	~6.41	~6.41
5a	1.99	4.96	5.20	3.04	~6.27	6.74	~6.41

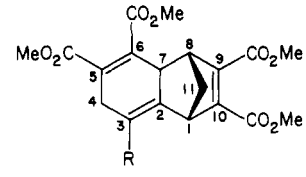
1- and 2-(1-Methylenepropyl)-1,3-cyclopentadiene (4b, 5b). (a) 5-(1-Methylpropylidene)-1,3-cyclopentadiene (1b). Butanone (14.4 g, 200 mmol), cyclopentadiene (19 mL, 200 mmol), sodium (4.6 g, 200 mmol), and ethanol (130 mL) were employed to give **1b** (14.4–16.8 g, 60–70%): bp 80–90 °C (15 torr); 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 4 H, ring), 2.53 (q, J = 7 Hz, 2 H, CH_2CH_3), 2.18 (s, 3 H, 1-CH_3), 1.14 (t, J = 7 Hz, 3 H, CH_2CH_3).

(b) 1b was isomerized as described for **1a**. **1b** (2.4 g, 20 mmol) gave **4b** and **5b** (1.9 g, 80%): 90-MHz ^{1}H NMR ($CDCl_3$) (inter alia) δ 1.1 (t, J = 7 Hz, 2 CH_3), 2.35 (m, J = 7 Hz, 2 CH_2), 3.04 (br, ring CH_2 of **5b**), 3.1 (m, ring CH_2 of **4b**), 4.8 + 5.1 (br, =CH_2 of **5b**).

Diels–Alder Reactions with Acetylenedicarboxylic Acid Dimethyl Ester. Vinylcyclopentadienes **4a/5a** (ca. 14 mmol) and **4b/5b** (ca. 14 mmol) were prepared in a solution of ca. 10 mL of pentane as described above. The solutions were cooled to 0 °C under N_2 and mixed dropwise with acetylenedicarboxylic acid dimethyl ester (3 g, 21 mmol). The solution was stirred and allowed to reach room temperature overnight. After removal of the solvent the remaining oil was chromatographed on silica gel (10:1 light petroleum/ether). The 1:1 adduct (**7a** and **7b**) was distilled (Kugelrohr) and the 2:1 adduct (**8a** and **8b**) was recrystallized from ether.



7a, R = Me
b, R = Et



8a, R = Me
b, R = Et

1-(1-Methylethenyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (7a): yield, 1.6 g (ca. 70% with respect to **4a**); bp 100–110 °C (0.5 torr); 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.96 (m, 2 H, 5-H and 6-H), 5.04 (br s, 2 H, 9-H), 4.0 (m, 1 H, 4-H), 3.78/3.73 (each s, 3 H, OCH_3), 2.48 [dd, J = 7 Hz, J = 1.5 Hz, 1 H, 7-H (5,6-double bond)], 2.13 [dd, J = 7 Hz, J = 1.5 Hz, 1 H, 7-H (2,3-double bond)], 1.84 (ca. t, 3 H, 8-CH_3); ^{13}C NMR ($CDCl_3$) δ 166.76/163.70 (each s, C=O), 159.34/147.84 (each s, C-2/C-3), 143.67/142.67 (each d, C-5/C-6), 141.55 (s, C-8), 113.35 (t, C-9), 75.0 (t, C-7), 71.79 (s, C-1), 51.85 (d, C-4), 51.85 (q, OCH_3), 50.95 (q, OCH_3), 21.60 (q, 8-CH_3); mass spectrum (70 eV), m/z (relative intensity) 248 (M^+, 29), 233 (9), 216 (100), 207 (10), 201 (19), 189 (56), 157 (36), 145 (15), 129 (53), 106 (55), 91 (66); exact mass calcd for $C_{14}H_{16}O_4$ m/z 248.10486, found 248.10365.

3-Methyltricyclo[6.2.1.0^{2,7}]undeca-2,5,9-triene-5,6,9,10-tetracarboxylic acid tetramethyl ester (8a): yield, 1.1 g (ca. 60%, with respect to **5a**); 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.93 (m, 1 H, 1-H), 3.86/3.80/3.79/3.76 (each s, 3 H, OCH_3), 3.28 (m, 1 H, 7-H), 2.67–3.10 (m, 3 H, 4-H and 8-H), 1.96 [m, 1 H, 11-H (9,10-double bond)], 1.90 (br s, 3 H, 3-CH_3), 1.44 (dt, J = 9.5 Hz, J = 1.5 Hz, 1 H, 11-H); ^{13}C NMR ($CDCl_3$) δ 168.36/165.87/164.90/164.39 (each s, C=O), 146.46/143.78/142.25/133.31/132.50/125.77 (each s, C-2/C-3/C-5/C-6/C-9/C-10), 52.25/52.14 (each q, OCH_3), 49.26 (t, C-11), 48.16 (d, C-1), 47.26 (d, C-7), 44.43 (d, C-8), 34.62 (t, C-4), 19.18 (q, 3-CH_3); mass spectrum (70 eV), m/z (relative intensity) 390 (M^+, 0), 358 (69), 343 (14), 299 (100), 267 (51), 259 (34), 239 (34), 177 (40), 152 (76). Anal. Calcd for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.47; H, 5.73.

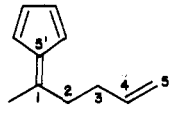
1-(1-Methylenepropyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (7b): yield; 1.7 g (ca. 70%, with respect to **4b**); bp 120–130 °C (0.5 torr); 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.96 (m, 2 H, 5-H and 6-H), 5.10/5.04 (each m, 2 H, 9-H), 3.99 (m, 1 H, 4-H), 3.76/3.72 (each s, 3 H, OCH_3), 2.48 [dd, J = 7 Hz, J = 1.5 Hz, 1 H, 7-H (5,6-double bond)], 2.14 [dd, J = 7 Hz, J = 1.5 Hz, 1 H, 7-H (2,3-double bond)/q, 2 H, 8-CH_2CH_3], 1.08 (t, J = 7 Hz, 3 H, 8-CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.73/163.72 (each s, C=O), 159.94/147.52 (each s, C-2/C-3), 147.30 (s, C-8), 143.59/142.92 (each d, C-5/C6), 110.99 (t, C-9), 75.24 (t, C-7), 72.13 (s, C-1), 51.90 (d, C-4), 51.83/80.83 (each q, OCH_3), 27.11 (t, 8-CH_2-CH_3), 12.27 (q, 8-CH_2-CH_3); mass spectrum (70 eV), m/z (relative intensity) 262 (M^+, 16), 247 (8), 230 (100), 215 (22), 203 (55), 187 (20), 171 (33), 143(45), 128 (30), 120 (40), 115 (27), 105 (36), 91 (53); exact mass calcd for $C_{15}H_{18}O_4$ m/z 262.12051, found m/z 262.11963.

3-Ethyltricyclo[6.2.1.0^{2,7}]undeca-2,5,9-triene-5,6,9,10-tetracarboxylic acid tetramethyl ester (8b): yield, 1.1 g (ca. 60%, with respect to **5b**); 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.94 (m,

(12) Crane, G.; Boord, C. E.; Henne, A. L. *J. Am. Chem. Soc.* **1945**, *67*, 1237.

1 H, 1-H), 3.86/3.80/3.78/3.76 (each s, 3 H, OCH_3), 3.29 (m, 1 H, 7-H), 2.61–3.15 (m, 3 H, 4-H and 8-H), 2.11–2.40 (m, 2 H, 3-CH_2-CH_3), 1.97 [m, 1 H, 11-H (9,10-double bond)], 1.44 (dt, J = 9.5 Hz, J = 1.5 Hz, 1 H, 11-H), 1.02 (t, J = 7 Hz, 3 H, 3-CH_2-CH_3); ^{13}C NMR ($CDCl_3$) δ 168.27/165.79/164.78/164.33 (each s, C=O), 146.28/144.07/142.44/133.65/132.38/131.80 (each s, C-2/C-3/C-5/C-6/C-9-C-10), 52.10/52.02 (each q, OCH_3), 49.23 (t, C-11), 47.98 (d, C-1), 47.16 (d, C-7), 44.59 (d, C-8), 32.45 (t, C-4), 26.77 (t, 3-CH_2CH_3), 13.14 (q, 3-CH_2CH_3); mass spectrum (70 eV), m/z (relative intensity) 404 (M^+, 0), 372 (57), 343 (30), 313 (100), 281 (37), 252 (39), 191 (41), 165 (47), 152 (39). Anal. Calcd for $C_{21}H_{24}O_8$: C, 62.36; H, 5.99. Found: C, 62.27; H, 5.95.

5′-(1-Methyl-4-pentenylidene)-1′,3′-cyclopentadiene (11a). Reaction of 5-hexen-2-one (9.8 g, 100 mmol), cyclopentadiene (9.5 mL, 100 mmol), and sodium (2.3 g, 100 mmol) in ethanol (80 mL) gave **11a**: yield, 7.3–8.8 g (50–60%); bp 80–90 °C (12 torr); 90-MHz



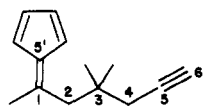
11a

^1H NMR ($CDCl_3$) δ 6.47 (s, 4 H, ring), 5.58–6.60 (ddt, J = 17 Hz, J = 10 Hz, J = 7 Hz, 1 H, 4-H), 4.84–5.20 (m, 2 H, 5-H), 2.49–2.76 (t, J = 7 Hz, 2 H, 3-H), 2.22–2.44 (m, 2 H, 2-H), 2.20 (s, 3 H, 1-CH_3); ^{13}C NMR ($CDCl_3$) δ 152.42 (s, C-1), 142.98 (s, C-5′), 137.52 (d, C-4), 130.95/130.77/120.71/120.35 (each d, ring), 115.24 (t, C-5), 36.26/33.26 (each t, C-2/C-3), 20.81 (q, 1-CH_3); mass spectrum (70 eV), m/z (relative intensity) 146 (M^+, 55), 131 (100), 117 (25), 105 (41), 91 (45).

5′-(1,5-Dimethyl-4-hexenylidene)-1′,3′-cyclopentadiene (11b). 6-Methylhept-5-en-2-one (25.2 g, 200 mmol), cyclopentadiene (19 mL, 200 mmol), and sodium (4.6 g, 200 mmol) in ethanol (130 mL) were allowed to react, giving **11b** (17.4–20.9 g, 50–60%): bp 120–130 °C (12 torr); 90-MHz ^1H NMR ($CDCl_3$) δ 6.49 (s, 4 H, ring), 5.13 (t, J = 7 Hz, 1 H, 4-H), 2.54 (t, J = 7 Hz, 2 H, 3-H), 2.28 (m, 2 H, 2-H), 2.21 (s, 3 H, 1-CH_3), 1.68 (br s, 3 H, 5-CH_3), 1.61 (br s, 3 H, 5-CH_3); ^{13}C NMR δ 152.76 (s, C-1), 142.92 (s, C-5′), 132.37 (s, C-5), 130.78/130.56 (each d, ring), 123.44 (d, C-4), 120.68/120.41 (each d, ring), 37.04/28.05 (each t, C-2/C-3), 25.65 [q, 5-CH_3 (trans)], 20.86 (q, 1-CH_3), 17.64 [q, 5-CH_3 (cis)]; mass spectrum (70 eV), m/z (relative intensity) 174, (M^+, 14), 159 (22), 131 (84), 91 (38), 69 (100).

5′-(1-Methyl-5-hexynylidene)-1′,3′-cyclopentadiene (11c). Reaction of 6-heptyn-2-one (2 g, 18 mmol), cyclopentadiene (1.7 mL, 18 mmol), sodium (0.4 g, 17.4 mmol) in ethanol (20 mL) gave **11c**: yield, 1.4–1.7 g (50–60%); bp 80 °C (0.5 torr); IR (CCl_4) 3320 vs, 2120 m, 1640 vs, 1620 m cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 6.49 (s, 4 H, ring), 2.64 (t, J = 7 Hz, 2 H, 2-H), 2.09–2.33 (m, 2 H, 4-H), 2.19 (s, 3 H, 1-CH_3), 1.99 (t, J = 2.5 Hz, 1 H, 6-H), 1.57–1.94 (m, 2 H, 3-H); ^{13}C NMR ($CDCl_3$) δ 151.97 (s, C-1), 143.31 (s, C-5′), 131.07/130.84/120.68/120.41 (each d, ring), 83.78 (s, C-5), 69.03 (d, C-6), 35.60 (t, C-2), 27.87 (t, C-3), 20.78 (q, 1-CH_3), 18.27 (t, C-4); mass spectrum (70 eV), m/z (relative intensity 158 (M^+, 36), 143 (68), 130 (50), 115 (40), 106 (57), 91 (100).

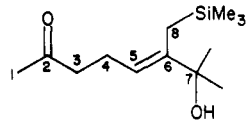
5′-(1,3,3-Trimethyl-5-hexynylidene)-1′,3′-cyclopentadiene (11d). Sodium hydride (75% in mineral oil, 2.1 g, 66 mmol) was washed with pentane (3×) under N_2 and then suspended in absolute THF (60 mL). Cyclopentadiene (5.7 mL, 60 mmol) was added at 0 °C, the mixture being stirred and allowed to reach room temperature during 30 min. 4,4-Dimethyl-6-heptyn-2-one[5] (2.8 g, 20 mmol) in absolute THF (10 mL) was added, the mixture being stirred overnight and poured onto an ice-cold saturated solution (150 mL) of ammonium chloride. After extraction with pentane (4 × 50 mL), the organic phase was washed with water (50 mL) and saturated aqueous NaCl and dried ($MgSO_4$). The solvent was evaporated and the remaining alkynone was distilled off [bp 50–60 °C (12 torr)] to leave an oil, which was chromatographed on neutral Al_2O_3 (activity II–III, light petroleum). **11d** was isolated as a bright yellow oil: 0.56 g, 15% yield; IR (CCl_4)



11d

3320 s, 2120 w, 1635 s, 1620 m cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 6.44 (m, 4 H, ring), 2.59 (s, 2 H, 2-H), 2.28 (s, 3 H, 1-CH_3), 2.16 (d, J = 2.5 Hz, 2 H, 4-H), 2.07 (t, J = 2.5 Hz, 1 H, 6-H), 1.06 (s, 6 H, 3-CH_3); ^{13}C NMR ($CDCl_3$) δ 150.34 (s, C-1), 145.59 (s, C-5′), 130.95/130.62/121.68/120.74 (each d, ring), 82.25 (s, C-5), 70.82 (d, C-6), 47.17 (t, C-2), 35.48 (s, C-3), 33.01 (t, C-4), 27.81 (q, 3-CH_3), 23.71 (q, 1-CH_3); mass spectrum (70 eV), m/z (relative intensity) 186 (M^+, 5), 171 (20), 156 (8), 147 (20), 143 (27), 130 (74), 115 (36), 106 (42), 91 (100), 79 (57).

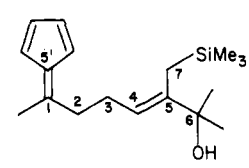
5′-[6-Hydroxy-1,6-dimethyl-5-[(trimethylsilyl)methyl]-4-heptenylidene]-1′,3′-cyclopentadiene (11e). (a) 7-Hydroxy-7-methyl-6-[(trimethylsilyl)methyl]-5-octen-2-one (10e). A solution of pyridine–SO_3 complex[7] (4.3 g, 27 mmol) in absolute Me_2SO (25 mL) was added dropwise to a mixture of diol **12** (2.2 g, 9 mmol) and triethylamine (12.5 mL, 90 mmol) in absolute Me_2SO under N_2 at room temperature. The temperature was maintained between 25–30 °C. After being stirred for 1 h at room temperature the mixture was poured onto ice–water (100 mL) and extracted with ether (2 × 70 mL). The aqueous phase was saturated with NaCl and reextracted with ether (2 × 50 mL). The combined ether phase was washed with aqueous 0.5 N $KHSO_4$ (100 mL) and a saturated solution (50 mL) of NaCl and dried ($MgSO_4$). After evaporation of the solvent the residue was chromatographed on neutral Al_2O_3 (activity IV, 5:1 light petroleum/ether) to give **10e** (1.1 g, 50%): IR (CCl_4) 3620 w, 3450 w,



10e

2960 m, 2900 m, 1725 s, 1365 m, 1250 s, 1160 m, 910 m, 855 s cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$, Me_4Si added afterwards) δ 5.22 (t, J = 7 Hz, 1 H, 5-H), 2.34 (m, 2 H, 4-H), 2.17–2.32 (t, J = 6 Hz, 2 H, 3-H), 2.13 (s, 3 H, 1-H), 1.63 (s, 2 H, 8-H), 1.30 (s, 6 H, 7-CH_3), 0.06 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 208.58 (s, C-2) 145.69 (s, C-6), 117.94 (d, C-5), 73.41 (s, C-7), 43.63 (t, C-4), 29.95 (q, 7-CH_3/C-1), 23.36 (t, C-3), 17.78 (t, C-8), 0.26 (q, $SiMe_3$); mass spectrum (70 eV), m/z (relative intensity) 242 (M^+, 0), 224 (2), 209 (5), 181 (2), 152 (5), 137 (11), 130 (14), 119 (11), 115 (59), 109 (64), 75 (68), 73 (100).

(b) A 1.6 N solution (6.3 mL) of n-butyllithium (10 mmol) in hexane was dropped to freshly distilled cyclopentadiene (1 mL, 10 mmol) in absolute THF (20 mL) at 0 °C under N_2. The mixture was stirred for 20 min, a white precipitate being formed. Hydroxyketone **10e** (1.1 g, 4.5 mmol) in absolute THF (10 mL) was added at 0 °C. The mixture was stirred for a further 2 h at room temperature and poured onto an ice-cold saturated solution (100 mL) of NH_4Cl. After extraction with ether (4 × 50 mL) and washing of the ether phase with a saturated NaCl solution (50 mL), the organic phase was dried ($MgSO_4$), freed from solvent, and chromatographed on neutral Al_2O_3 (activity IV, 20:1 light petroleum/ether) to give **11e** (0.65–0.78 g, 50–60%): IR (CCl_4)



11e

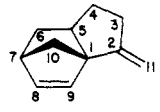
3500 w, 1635 s, 1470 m, 1365 s, 1250 s, 1155 s, 1040 s, 840 vs cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$, Me_4Si added afterwards) δ 6.51 (br s, 4 H, ring), 5.32 (t, J = 7 Hz, 1 H, 4-H), 2.49–2.73 (ca. t, 2 H, 3-H), 2.11–2.37 (m, 2 H, 2-H), 2.24 (s, 3 H, 1-CH_3), 1.64 (br s, 2 H, 7-H), 1.33 (s, 6 H, 6-CH_3), 0.07 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 152.99 (s, C-1), 145.46 (s, C-5), 143.06 (s, C-5′), 131.00/130.78/120.85/120.67 (each d, ring), 118.73 (d, C-4), 73.56 (s, C-6), 36.89 (t, C-3), 29.92 (q, 6-CH_3), 28.55 (t, C-2), 21.14 (q, 1-CH_3), 17.83 (t, C-7), 0.35 (q, $SiMe_3$); mass spectrum (70 eV), m/z (relative intensity) 290 M^+, 0), 272 (2), 257 (2), 200 (6), 185 (14), 172 (13), 157 (23), 143 (16), 131 (19), 117 (11), 105 (9), 95 (37), 73 (100).

Isomerization of 11a–e (Chart II) and Intramolecular Cycloadditions (Chart III). The isomerization was carried out

as for **4a/5a**. Fulvenes **11a + 11b** (19.5 mmol each) were isomerized and worked up as described. Fulvenes **11c–e** required 2 equiv of LDA in double the quantity of solvent (20 mmol of fulvene in 60 mL of THF). **13eα** and **13eβ** were isolated after quenching with aqueous NaH_2PO_4 instead of 1 N HCl.

The vinylcyclopentadienes **13a–d** were freed from the bulk of solvent in vacuo and dropped under N_2 with vigorous stirring into ethylene glycol (150 mL) at 190 °C. After being stirred at 190 °C for 1 h, the reaction mixture was cooled to room temperature, poured into water (300 mL), and extracted with pentane (4 × 100 mL). The combined organic phase was washed with a saturated solution of NaCl, dried ($MgSO_4$), and freed from solvent. The product was purified by distillation (Kugelrohr) and chromatography (silica gel/light petroleum).

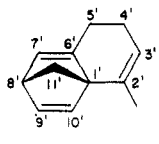
2-Methylenetricyclo[5.2.1.0^{1,5}]dec-8-ene (14a). **14a** (0.3 g, 20% with respect to **13aα**) and **11a** (0.4–0.7 g, ca. 20–30% with respect to isomeric mixture **13aα,β**) were obtained after chromatography. **14a**: 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.10 (m, 2 H, 8-H



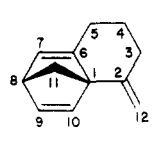
14a

and 9-H), 4.94 (m, 2 H, 11-H), 2.97 (br s, 1 H, 7-H), 2.47–2.74 (m, 2 H, 3-H), 1.88–2.23 (m, 1 H, 5-H), 1.14–1.85 (m, 6 H, 4-H, 6-H, and 10-H); ^{13}C NMR ($CDCl_3$) δ 151.91 (s, C-2), 139.40/136.19 (each d, C-8/C-9), 105.44 (t, C-11) 66.37 (s, C-1), 53.95 (t, C-10), 46.59/46.19 (each d, C-5/C-7), 34.86/33.53/31.29 (each t, C-3/C-4/C-6); mass spectrum (70 eV), *m/z* (relative intensity) 146 (M^+, 85), 131 (100), 117 (42), 105 (28), 91 (60); exact mass calcd for $C_{11}H_{14}$ *m/z* 146.10955, found *m/z* 146.10825.

2-Methyltricyclo[6.2.1.0^{1,6}]undeca-2,6,9-triene (14cα) and 2-methylenetricyclo[6.2.1.0^{1,6}]undeca-6,9-diene (14cβ): Yield of **14cα + 14cβ**, 0.1 g (13% with respect to **13cα**; **14cα**:**14cβ** = 2:1); yield of **11c**, 0.25–0.38 g (ca. 20–30% with respect to isomeric



14cα



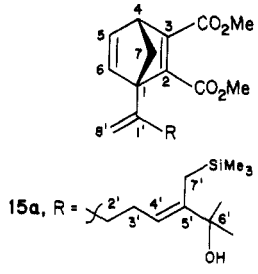
14cβ

mixture **13cα,β**); [**14cα,β**] (endo/exo mixture) 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.69 (m, 2 H, 9-H and 10-H, respectively, 9′-H and 10′H), 6.14 (m, 1 H, 7-H and 7′-H), 5.63 (m, 1 H, 3′-H), 4.84 (ca. t, 1 H, 12-H), 4.70 (ca. t, 1 H, 12-H), 3.52 (m, 1 H, 8-H and 8′-H), 1.81–2.79 (m, ca. 6 H, 3-H, 4-H, 5-H, and 4′-H, 5′-H, 11′-H/11-H), 1.76 (br s, 3 H, 2′-CH_3); ^{13}C NMR ($CDCl_3$) δ 156.45/155.82 (each s, C-6/C-6′), 150.10 (s, C-2), 146.53/144.28/143.55/142.80 (each d, C-9/C-10/C-9′/C-10′), 134.47 (s, C-2′), 132.22/131.16 (each d, C-7/C-7′), 123.41 (d, C-3′), 108.27 (t, C-12), 76.01/75.64 (each t, C-11/C-11′), 64.48/63.28 (each s, C-1/C-1′), 49.30/48.87 (each d, C-8/C-8′), 34.53/27.51/25.26/25.16/25.02 (each t, C-3/C-4/C-5/C-4′/C-5′), 20.18 (q, 2′-CH_3); mass spectrum (70 eV), *m/z* (relative intensity) 158 (M^+, 93), 143 (100), 128 (70), 117 (48), 91 (32); exact mass calcd for $C_{12}H_{14}$ *m/z* 158.10955, found *m/z* 158.10992.

4,4-Dimethyl-2-methylenetricyclo[6.2.1.0^{1,6}]undeca-6,9-diene (14d): yield of **14d**, 0.15 g (30% with respect to **13dα**); yield of **11d**, 0.08–0.12 g (ca. 10–15% with respect to isomeric mixture **13dα,β**); [**14d**] 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.66 (m, 2 H, 9-H and 10-H), 6.12 (ca. 1 H, 7-H), 4.81 (m, 2 H, 12-H), 3.53 (m, 1 H, 8-H), 2.11–2.48 (m, 4 H, 3-H and 5-H and 11-H), 1.70–1.98 (m, 2 H, 3-H/5-H and 11-H), 1.03/0.79 (each br s, 3 H, 4-CH_3); ^{13}C NMR ($CDCl_3$) δ 155.52 (s, C-6), 148.24 (s, C-2), 146.47/142.82 (each d, C-9/C-10), 133.01 (d, C-7), 109.90 (t, C-12), 75.72 (t, C-11), 63.68 (s, C-1), 49.26 (d, C-8), 48.41/41.50 (each t, C-3/C-5), 31.74 (s, C-4), 31.08/25.44 (each q, 4-CH_3); mass spectrum (70 eV), *m/z* (relative intensity) 186 (M^+, 100), 171 (75), 160 (47), 145 (55), 143 (65), 130 (79), 115 (42), 91 (34); exact mass calcd for $C_{14}H_{18}$ *m/z* 186.14085, found *m/z* 186.14086.

Characterization of 13eα,β via Cycloaddition with Acetylenedicarboxylic Acid Dimethyl Ester (Scheme V). After the usual deprotonation of fulvene **11e** (0.2 g, 0.7 mmol) and quenching with aqueous NaH_2PO_4, the solvent pentane was removed down to 5 mL. The solution was added to an excess of acetylenedicarboxylic acid dimethyl ester in absolute ether and stirred overnight. After removal of the solvent the residue was chromatographed on neutral Al_2O_3 (activity IV, 1:1 light petroleum/ether), giving **15a** and **15b** as yellowish oils.

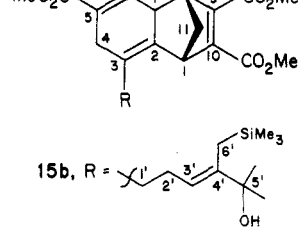
1-[6′-Hydroxy-6′-methyl-5′-[(trimethylsilyl)methyl]-1′-methylene-4′-heptenyl]bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (15a): yield, 0.1 g (ca, 70% with



15a, R =

respect to **13eα**); IR (CCl_4) 3620 w, 3500 w, 2960 m, 1720 s, 1630 m, 1440 m, 1250 s, 1110 m, 850 m cm^{-1}; 90-MHz ^{1}H NMR ($CDCl_3$) δ 6.89 (m, 2 H, 5-H and 6-H), 5.19–5.44 (m, 1 H, 4′-H), 5.08/5.0 (each br s, 1 H, 8′-H), 3.87–4.0 (m, 1 H, 4-H), 3.69 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 2.33–2.48 [dd, *J* = 7 Hz, *J* = 1.5 Hz, 1 H, 7-H) (5,6-double bond)], 2.03–2.18 [m, 5 H, 2′-H, 3′-H and 7-H (2,3-double bond)], 1.59 (br s, 2 H, 7′-H), 1.26 (s, 6 H, 6′-CH_3), 0.03 (s, 9 H, $SiMe_3$); mass spectrum (70 eV), *m/z* (relative intensity) 432 (M^+, O), 417 (6), 401 (3), 385 (5), 342 (38), 327 (9), 310 (13), 295 (18), 241 (24), 185 (17), 171 (35), 158 (27), 131 (43), 73 (100); exact mass calcd for $C_{23}H_{33}O_5Si$ *m/z* 417.20973, found *m/z* 417.20716.

3-[5′-Hydroxy-5′-methyl-4′-[(trimethylsilyl)methyl]-3′-hexenyl]tricyclo[6.2.1.0^{2,7}]undeca-2,5,9-triene-5,6,9,10-tetracarboxylic acid tetramethyl ester (15b): yield, 0.06 g (ca. 60%



15b, R =

with respect to **13eβ**); IR (CCl_4) 3620 w, 3500 w, 2960 m, 1730 s, 1630 m, 1440 m, 1260 s, 850 m cm^{-1}; 90-MHz 1H NMR ($CDCl_3$) δ 5.26 (t, *J* = 6 Hz, 1 H, 3′-H), 3.97 (m, 1 H, 1-H), 3.86/3.80/3.79/3.76 (each s, 3 H, OCH_3), 2.60–3.38 (m, 4 H, 4-H, 8-H, 7-H), 1.89–2.49 [m, 5 H, 1′-H, 2′-H and 11-H (9,10-double bond)], 1.62 (br s, 2 H, 6′-H), 1.36–1.57 (m, 1 H, 11-H), 1.30 (br s, 6 H, 5′-CH_3), 0.06 (s, 9 H, $SiMe_3$); mass spectrum (70 eV), *m/z* (relative intensity) 574 (M^+, 0), 559 (3), 557 (2), 556 (4), 543 (3), 541 (3), 527 (6), 525 (5), 524 (4), 452 (14), 420 (16), 393 (31), 371 (100), 369 (99), 357 (66), 73 (700% of 371).

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Registry No. **1a**, 2175-91-9; **1b**, 3141-02-4; **4a**, 26385-00-2; **4b**, 100940-15-6; **5a**, 26385-01-3; **5b**, 59108-98-4; **7a**, 100940-16-7; **7b**, 100940-18-9; **8a**, 100940-17-8; **8b**, 100940-19-0; **10a**, 109-49-9; **10b**, 110-93-0; **10c**, 928-39-2; **10d**, 17520-15-9; **10e**, 100940-22-5; **11a**, 71546-85-5; **11b**, 64243-15-8; **11c**, 100940-20-3; **11d**, 100940-21-4; **11e**, 100940-24-7; **12**, 100940-23-6; **13aα**, 100940-25-8; **13aβ**, 100940-26-9; **13bα**, 100940-27-0; **13bβ**, 100940-28-1; **13cα**, 100940-29-2; **13cβ**, 100940-30-5; **13dα**, 100940-31-6; **13dβ**, 100940-32-7; **13eα**, 100940-33-8; **13eβ**, 100940-34-9; **14a**, 100940-35-0; **14b**, 100940-36-1; **14cα**, 100940-37-2; **14cβ**, 100940-38-3; **14d**, 100940-39-4; **15a**, 100940-40-7; **15b**, 100940-41-8; 2-butanone, 78-93-3; dimethyl acetylenedicarboxylate, 762-42-5; cyclopentadiene, 542-92-7.