Stereoselective Synthesis of α,β-*trans*-Spiro-β-lactones by Diels-Alder Cycloaddition of 1,3-Dienes to α-Methylene-β-lactone and Their Decarboxylation by Pyrolysis to (*E*)-Alkylidenecycloalkenes, a Convenient Olefination Method

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A number of spiro-β-lactones was prepared in good to excellent yields through stereoselective [4 + 2] cycloaddition of β-isopropyl-α-methylene-β-lactone (**1**) with acyclic, cyclic, heterocyclic and aromatic 1,3-dienes by sealed-tube reaction at moderate temperatures (50 – 130 °C). Flash pyrolysis of the resulting spiro-β-lactones **2** in the gas phase at 400 °C afforded by decarboxylation exclusively the corresponding (*E*)-isopropylidenealkenes in high yields with retention of the initial geometry and without double bond isomerization. This olefination method constitutes an excellent stereoselective synthesis of (*E*)-alkylidenecycloalkenes.

Stereoselective Diels-Alder cycloadditions are presently in the focus of attention in asymmetric synthesis[1]. Assistance through chiral auxiliaries, which are incorporated into the substrate and subsequently removed from the cycloadduct by some chemical means, is one of the most popular methods to achieve stereocontrol in [4 + 2] cycloadditions. Among such chiral auxiliaries, which control stereoselectivity efficiently in these cycloadditions, figure hydrosuccinimides[2], pantolactones[3], and amino acids[4]. On the other hand, the use of chiral dienophiles is an excellent way to perform stereocontrol, e.g. the cycloaddition of 2-alkyl-5-methylene-4-dioxolanones with cyclopentadiene to give the α,γ-*trans*-*exo*-cycloadducts[5].

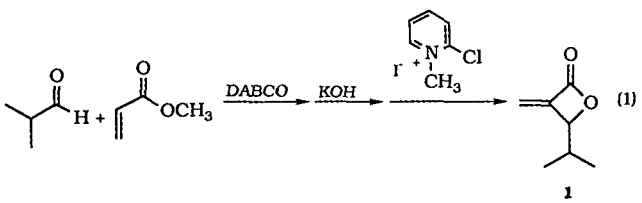
The ready availability of the α-methylene-β-lactone **1** by various methods[6] and especially its numerous reaction modes as allene equivalent[7] make this dienophile an attractive synthetic intermediate in organic chemistry. For example, recently we reported[7,8] that β-lactone **1** reacts stereoselectively with cyclopentadiene to afford exclusively the spiro-β-lactones *exo*- and *endo*-**2c** in good yields (50 – 70%). The stereogenic center at the β carbon atom of the α-methylene-β-lactone provides the high stereoselectivity in the [4 + 2] cycloaddition without assistance of an additional chiral auxiliary. On pyrolysis the spiro-β-lactones decarboxylate smoothly to the corresponding alkenes.

On the other hand, alkyl-substituted allenes display as dienophiles poor regio- and stereoselectivity. Furthermore, particularly their sluggish reactivity presents difficulties for synthetic applications. For this reason a number of allene equivalents have been developed[9].

Presently, we elaborate this convenient olefination method by employing the α-methylene-β-lactone **1** as a useful allene equivalent in [4 + 2] cycloaddition reactions. Thus, the cycloaddition of a variety of dienes, which includes the acyclic cases 1,3-butadiene and isoprene, the cyclic derivatives cyclopentadiene and 1,3-cyclohexadiene, the arene anthracene, and the heteroarene furan to α-methylene-β-lactone **1** affords the spiro-β-lactones **2**. Subsequent pyrolysis leads to the (*E*)-alkylidenecycloalkenes by decarboxylation[10].

Results and Discussion

The α-methylene-β-lactone **1** can be obtained either from the deoxygenation of the corresponding β-peroxylactone[6c] or from the direct cyclization of 3-hydroxy-4-methyl-2-methylenepentanoic acid[11] by using benzylsulfonyl chloride in pyridine. A new and more effective cyclization reagent for the strained β-lactone turned out to be 2-chloro-1-methylpyridinium iodide[12] in the presence of triethylamine, which yielded **1** in 62% overall yield by starting from acrylic ester and 2-methylpropanal (Eq. 1).



(1)

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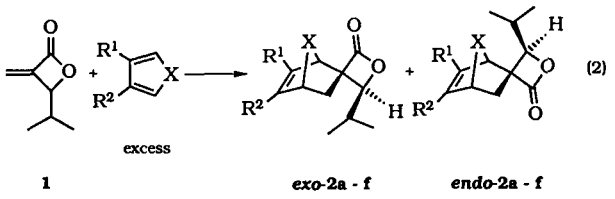
The [4 + 2] cycloaddition of the α-methylene-β-lactone **1** with cyclopentadiene has been described already in a previous paper, in which $Ti(OiPr)_4$ was used as catalyst[7,8]. Unfortunately, this method was not effective for the less reactive

dienes employed here. The use of stronger Lewis acids than $Ti(OiPr)_4$, e.g. $AlCl_3$ or $CpZrCl_3(THF)_2$, promoted the rearrangement of **1** to γ,γ-dimethyl-α-methylene-γ-lactone. Therefore, a more effective procedure consisted of heating the lactone **1** and an excess of the respective diene in a sealed tube at 50–130°C, and after chromatographic workup the spiro-β-lactones **2** were obtained in good yields (Eq. 2). The results of the Diels-Alder reactions are summarized in Table 1, in which the respective reaction conditions and yields are shown.



(2)

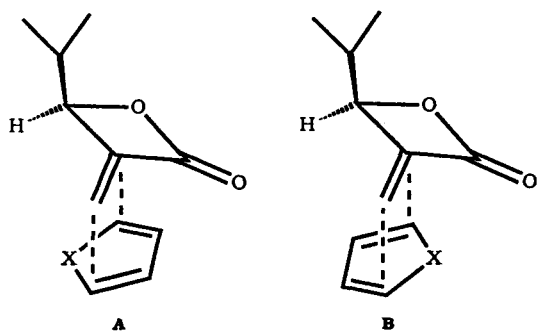
Diene	R^1	R^2	X	Products
Butadiene	H	H	H H	**a**
Isoprene	H	CH_3	H H	**b**
Cyclopentadiene	H	H	CH_2	**c**
Furan	H	H	O	**d**
1,3-Cyclohexadiene	H	H	$[CH_2]_2$	**e**
Anthracene	$[CH]_4$			**f**

Table 1. Diels-Alder cycloadditions of α-methylene-β-lactone **1** with dienes

Product	Temp. [°C]	Time[a] [h]	Ratio *exo/endo*	Yield[b] (%)
2a	130	24	-	54
2b	130	36	-	52
2c	50	24	71:29	94
2d	70[c]	216[d]	70:30	52[e]
2e	130	48	80:20	73
2f	130	108[f]	-	66

[a] For 100% conversion. — [b] Isolated yield after column chromatography. — [c] Decomposition at higher temperatures. — [d] 81% conversion. — [e] Isolated yield after distillation (50°C/10^{-5} Torr). — [f] 64% conversion.

Acyclic dienes like 1,3-butadiene and isoprene react with the α-methylene-β-lactone **1** at elevated temperatures with preservation of the β-lactone moiety. As products, only the spiro-β-lactones **2a**, **b** were observed as the result of the diastereoselective attack on the dienes from the less hindered side of the lactone **1** (transition states **A** and **B**).



In the case of the cycloaddition with isoprene, the major product was the "*para*" cycloadduct, as expected from the established regiochemistry for Diels-Alder reactions[13]. Only traces (<5%) of the corresponding "*ortho*" cycloadduct were detected by ^1H NMR.

As in the case of the acyclic dienes, the cycloaddition of the α-methylene-β-lactone **1** with cyclic dienes afforded only the spiro-β-lactones **2c–e** as products of the high diastereofacial *endo* and *exo* attack opposite to the β-isopropyl substituent, which is exhibited in the transition state structures **A** and **B**. Compared to cyclopentadiene, which undergoes cycloaddition in excellent yield already at 50°C, cyclohexadiene requires more drastic reaction conditions. The cycloaddition with furan, on the other hand, must be carried out at moderate temperature for much longer reaction time to obtain an acceptable yield of product **2d**.

For all cyclic dienes **2c–e** the dominant *exo* attack was observed as a result of steric interactions between the α-alkyl substituent of the α,β-unsaturated carbonyl dienophile and the aliphatic protons of the cyclodienes[14], although favored *endo* attack would be expected on account of secondary orbital interactions[15].

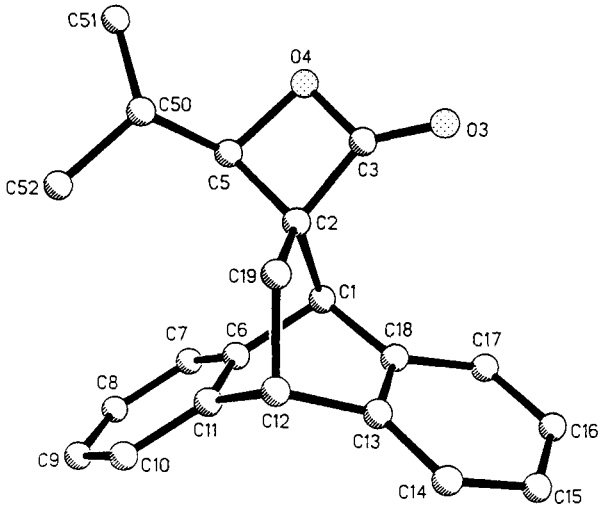


Figure 1. Structure of **2f** in the crystal; selected bond lengths [pm] and angles [°]: C1–C2 157.0(2), C2–C5 155.7(2), C3–O3 119.4(2), O4–C5 149.0(2), C2–C3 151.3(2), C2–C19 154.4(2), C3–O4 136.7(2), C5–C50 151.5(2); C1–C2–C5 111.5(1), C1–C2–C19 109.0(1), C5–C2–C19 121.7(1), C2–C3–O4 95.9(1), C3–O4–C5 91.3(1), C2–C5–C50 122.2(1), C1–C2–C3 112.1(1), C3–C2–C5 83.5(1), C3–C2–C19 117.0(1), C2–C3–O3 138.3(2), O3–C3–O4 125.8(2), C2–C5–O4 89.2(1), O4–C5–C50 111.8(1)

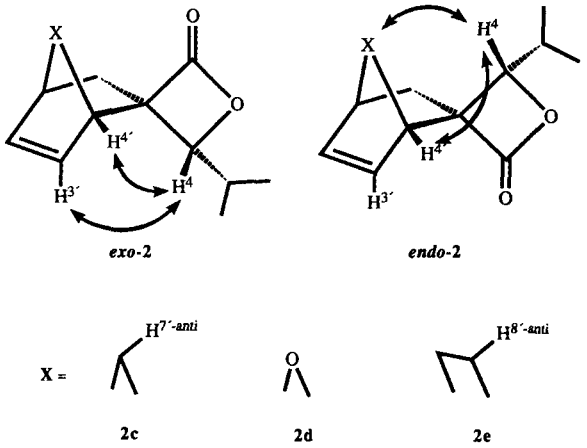
As expected, anthracene as diene partner showed a significantly lower reactivity towards the α-methylene-β-lactone **1**. A temperature as high as 130°C was required to afford exclusively the spiro-β-lactone **2f** (64% conversion) after 4.5 d. The α,β-*trans* stereochemistry of the cycloadduct **2f** was confirmed by an X-ray crystal structure analysis (Figure 1). The distorted square of this spiro-β-lactone has the bond angles C2–C3–O4 95.9°, C3–O4–C5 91.3°,

C3–C2–C5 83.5° and C2–C5–O4 89.2°, and the isopropyl group is clearly pointing towards the aromatic ring.

The structures of the new [4 + 2] cycloadducts **2a–e** were determined by NOE experiments. Thus, on irradiation of the β-lactone methinyl protons of the cycloadducts **2a, b** the signal of the allylic protons next to the β-lactone ring were enhanced and vice versa. The "*para*"regiochemistry of the cycloadduct **2b** was established through enhancement of the signals of the allylic protons next to the β-lactone ring by irradiation of the vinylic proton and its inverse effect.

For the cycloadducts **2c–e** the NOE results are summarized in Table 2. Enhancements of the signals of the vinylic and bridgehead protons $H^{3'}$ and $H^{4'}$ was observed on irradiation of the methinyl β-lactone proton H^4 and vice versa. These results definitively establish the α,β-*trans-exo* stereochemistry of these cycloadducts. On the other hand, the *endo* cycloadducts **2c–e** showed on irradiation of the β-lactone methinyl proton H^4 enhancements of the signals of the bridgehead proton $H^{4'}$ and the protons $H^{7'\text{-}anti}$ of **2c** and $H^{8'\text{-}anti}$ of **2e**, but none for **2d**.

Table 2. NOE effects for the tricyclic spiro-β-lactones **2c–e**



β-Lactone	Observed enhancements (%)[a]					
	4 → 3'	3' → 4	4 → 4'	4' → 4	4 → X	X → 4
***exo*-2c** [b]	2.5	1.8	2.1	2.2	-	-
***endo*-2c** [b]	-	-	3.6	6.2	1.1	-
***exo*-2d**	1.4	2.1	2.7	2.4	-	-
***endo*-2d**	-	-	1.9	2.6	-	-
***exo*-2e**	0.9	1.0	4.9	5.6	-	-
***endo*-2e**	-	-	3.4	5.4	0.8	2.7

[a] Arrow points from irradiated proton to the enhanced proton. – [b] Data from ref.[8].

Like for the acyclic, the [4 + 2] cycloaddition with the cyclic dienes leads only to the α,β-*trans* diastereoisomers **2c–f**. Thus, again the favored attack of the diene results from the face opposite of the isopropyl group (transition states **A** and **B**).

With a convenient spiro-β-lactone synthesis on hand, it was our interest to demonstrate the usefulness of these compounds as synthetic intermediates for the fixation of double bonds in carbon skeletons. Except for **2d**, which decomposes already at temperatures somewhat higher than 70°C, all spiro-β-lactones were pyrolyzed at 400°C and gave the respective cycloalkenes **3a–f** in excellent yields (Eq. 3 and Table 3).

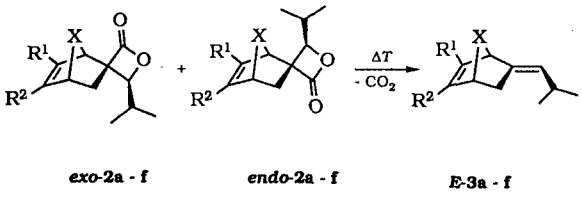


Table 3. Decarboxylation[a] of spiro-β-lactones **2a–f** to the olefins **3a–f**

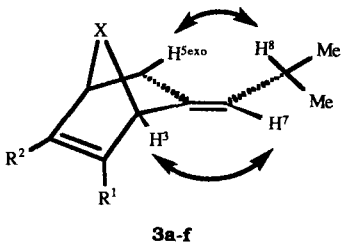
β-Lactone	Olefin	Yield[b] (%)
2a	**3a**	99
2b	**3b**	92
2c	**3c**	71
2e	**3e**	79
2f	**3f**	94[c]

[a] Thermolysis in the gas phase at 400°C. – [b] Determined by gas chromatography of the crude product mixture. – [c] Isolated yield after column chromatography.

The fact that exclusively the (*E*)-alkenes were obtained establishes that no isomerization had taken place under the decarboxylation conditions. Since the Wittig reaction for the introduction of alkylidene groups in comparable compounds works usually in modest yields to afford (*E*)/(*Z*) mixtures of alkenes[16], an attractive method for the diastereoselective synthesis of alkylidene-substituted cycloalkenes has been made available.

The stereochemical assignment of the cycloalkenes **3a–f** was also achieved through NOE experiments, which are

Table 4. NOE effects of the olefins **3a–f**



Olefin	Observed enhancements[a]			
	3 → 7	7 → 3	5 → 8	8 → 5
3a	10.3	0.6	5.1	2.2
3b	12.9	0.7	2.1	3.9
3c [b]	4.7	3.4	2.2	1.7
3e	9.1	6.0	4.1	3.1
4f	15.8	13.1	7.3	2.0

[a] Arrow points from irradiated proton to the enhanced proton. – [b] Data from ref.[8].

shown in Table 4. The (*E*) configuration of the semicyclic C=C bond was definitively established by irradiation of the exocyclic vinyl protons H^7, which enhanced the signals of the allylic protons H^3 and vice versa. Irradiation of the methinyl proton H^8 of the isopropyl group caused a signal enhancement of the allylic protons H^5 with the corresponding inverse effect.

In summary, it is our contention that the thermal decarboxylation of spiro-β-lactones, which are now readily prepared by [4 + 2] cycloaddition of α-methylene-β-lactone **1** with dienes, constitutes a useful stereoselective synthesis of alkylidene-substituted cycloalkenes. In this sense, the novel α-methylene-β-lactones of type **1** represent convenient allene equivalents, which are considerably more reactive dienophiles than substituted allenes with the additional advantage that the alkylidene functionalization proceeds regioselectively.

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Experimental

Instrumentation: Melting points: Büchi 535. – IR: Perkin-Elmer 1420. – ^1H and ^{13}C NMR: Bruker WM 250 (250 MHz). – NOE: Bruker WM 200 (200 MHz) or WM 400 (400 MHz); chemical shifts refer to TMS for ^1H and $CDCl_3$ for ^{13}C NMR. – MS. Varian MAT; Finnigan MAT (70 eV). – Analytic gas chromatography: Carlo Erba 2900 [Carbowax 20M, 30 m (I.D. = 0.25 mm); 0.8 atm He pressure; injector and detector temperature 175°C, initial temperature 50°C, temperature/time gradient 25°C/min, final temperature 120°C]. – Preparative gas chromatography: Carlo Erba 4200 [10% Carbowax 20M on Volaspher 2A, 3m; injector and detector temperatures 160°C, initial temperature 70°C, temperature/time gradient 5°C/min, final temperature 130°C]. – Boiling range of petroleum ether: 30–50°C.

4-(1-Methylethyl)-3-methylene-1-oxetane-2-one (**1**): To 2-chloro-1-methylpyridinium iodide (21.0 g, 82.0 mmol) in dry dichloromethane (400 ml) was added under N_2 a solution of 3-hydroxy-4-methyl-2-methylenepentanoic acid (4.00 g, 27.7 mmol) and triethylamine (30.5 ml, 222 mmol) in dichloromethane (200 ml). The resultant mixture was heated under reflux for 36 h, the solvent was removed by distillation (20°C/20 Torr) and the solid residue extracted with petroleum ether. The extracts were concentrated at reduced pressure, and after column chromatography [silica gel, petroleum ether/CH_2Cl_2 (1:1)] 2.98 g (85%) of **1** was obtained as a colorless liquid. The spectral data were in agreement with the data described in the literature[4].

General Procedure for the Diels-Alder Reactions of **1** *with 1,3-Dienes:* A solution of freshly distilled diene (usually an excess), **1** (200 mg, 1.58 mmol), and a trace (ca. 10 mg) of hydroquinone (to inhibit radical polymerization) was heated in a sealed tube until no starting material was detected. The excess of the diene was evaporated (20°C/20 Torr) and the residue was purified by column chromatography to yield the cycloadducts in 54–94%. Conditions are given in Table 1, and the details of the individual reactions are described below.

Spiro-β-lactone **2a**: According to the general procedure, by starting from 2.00 g (37.0 mmol) of butadiene, there was obtained 154 mg (54%) of **2a** after column chromatography [silica gel; petroleum ether/CH_2Cl_2 (1:1)] as a colorless amorphous solid, m.p. 44–45°C. – IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1}, 1828, 1660. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (d, *J* = 6.5 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 1.80 (m, 1H), 2.06 (dsept, *J* = 6.5 and 10.7 Hz, 1H), 2.10–2.60 (m, 5H), 3.76 (d, *J* = 10.7 Hz, 1H), 5.59–5.72 (m, 1H), 5.75–5.88 (m, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 17.6 (q), 19.2 (q), 22.5 (t), 23.1 (t), 28.2 (d), 31.7 (t), 55.3 (s), 87.44 (d), 122.5 (d), 127.8 (d), 174.02 (s). – $C_{11}H_{16}O_2$ (180.2): calcd. C 73.29, H 8.94; found C 73.60, H 9.12.

Spiro-β-lactone **2b**: According to the general procedure, by starting from 2.00 g (29.0 mmol) of isoprene, there was obtained 160 mg (52%) of **2b** after column chromatography [silica gel; petroleum ether/CH_2Cl_2 (1:1)] as a colorless, amorphous solid, m.p. 76–78°C. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 1825, 1720. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (d, *J* = 6.5 Hz, 3H), 1.05 (d, *J* = 6.4 Hz, 3H), 1.70 (s, 3H), 1.82 (ddd, *J* = 5.7, 10.7 and 12.7 Hz, 1H), 2.05 (dsept, *J* = 6.5 and 10.6 Hz, 1H), 2.90 (m, 1H), 2.25–2.55 (m, 4H), 3.76 (d, *J* = 10.7 Hz, 1H), 5.34 (br. s, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 17.7 (q), 19.2 (q), 23.2 (q), 23.5 (d), 27.2 (t), 28.3 (d), 32.0 (t), 55.2 (s), 87.2 (d), 116.6 (d), 135.0 (s), 174.2 (s). – $C_{12}H_{18}O_2$ (194.3): calcd. C 74.19, H 9.34; found C 73.76, H 9.65.

*Spiro-β-lactones exo-, endo-***2c**: According to the general procedure, by starting from 314 mg (4.70 mmol) of cyclopentadiene, there was obtained 204 mg of *exo-***2c** and 83.0 mg of *endo-***2c** (94%) after column chromatography [silica gel, heptane/ethyl acetate (9:1)]; *exo-***2c** is a colorless, amorphous solid (m.p. 28–30°C) and *endo-***2c** a colorless oil. The *exo/endo* ratio was 71:29, as determined by integration of the β-lactone protons *exo*-H [δ = 3.83 (d)] and *endo*-H [δ = 3.98 (d)] in the NMR spectrum of the crude product mixture. The spectral data are in agreement with those reported[7].

*Spiro-β-lactones exo-, endo-***2d**: According to the general procedure, by starting from 5.00 g (73.0 mmol) of furan, there was obtained 159 mg (52%) of *exo-***2d** and *endo-***2d** after distillation (50°C/10^{-5} Torr) as colorless, amorphous solid, m.p. 59–61°C. Also 18.0 mg of **1** was recovered (81% conversion). The *exo/endo* ratio was 70:30, as determined by integration of the β-lactone protons *exo*-H [δ = 4.18 (d)] and *endo*-H [δ = 3.83 (d)] in the NMR spectrum of the crude product mixture. – IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1}, 1840, 1700. – $C_{11}H_{14}O_3$ (194.2): calcd. C 68.02, H 7.26; found C 68.35, H 7.35.

*exo-***2d**: ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.96 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.65 (d, *J* = 12.3 Hz, 1H), 1.89 (dsept, *J* = 6.5 and 9.2 Hz, 1H), 2.21 (dd, *J* = 4.6 and 12.1 Hz, 1H), 4.18 (d, *J* = 9.3 Hz, 1H), 5.08 (d, *J* = 1.1 Hz, 1H), 5.10 (dd, *J* = 1.5 and 3.9 Hz, 1H), 6.45 (dd, *J* = 1.5 and 5.7 Hz, 1H), 6.58 (dd, *J* = 1.6 and 5.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 17.7 (q), 17.9 (q), 30.1 (d), 32.1 (t), 61.3 (s), 79.1 (d), 84.3 (d), 86.7 (d), 132.0 (d), 138.5 (d), 172.5 (s).

*endo-***2d**: ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.75 (d, *J* = 6.6 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H), 1.70 (d, *J* = 12.2 Hz, 1H), 1.77 (dsept, *J* = 6.6 and 9.3 Hz, 1H), 2.29 (dd, *J* = 4.5 and 12.1 Hz, 1H), 3.83 (d, *J* = 9.2 Hz, 1H), 5.20 (br. s, 1H), 5.22 (d, *J* = 8.34 Hz, 1H), 6.37 (dd, *J* = 1.6 and 5.7 Hz, 1H), 6.60 (dd, *J* = 1.7 and 5.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 18.0 (q), 18.3 (q), 30.7 (d), 31.4 (t), 61.0 (s), 78.8 (d), 81.2 (d), 81.8 (d), 132.9 (d), 139.8 (d), 174.2 (s).

*Spiro-β-lactones exo-, endo-***2e**: According to the general procedure, by starting from 381 mg (4.70 mmol) of cyclohexadiene, there was obtained 190 mg of *exo-***2e** and 48.0 mg of *endo-***2e** (73%) after column chromatography [silica gel; heptane/ethyl acetate (9:1)] as colorless oil and amorphous solid. The *exo/endo* ratio was 80:20, as determined by integration of the β-lactone protons *exo*-H

[δ = 3.73 (d)] and *endo*-H [δ = 3.92 (d)] in the NMR spectrum of the crude product mixture.

exo-**2e**: IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1}, 1820, 1710. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.77 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.18–1.29 (m, 2H), 1.57–1.75 (m, 3H), 1.80 (dd, *J* = 2.1 and 13.7 Hz, 1H), 2.18 (dt, *J* = 2.5 and 9 Hz, 1H), 2.68 (br. s, 1H), 2.89 (br. s, 1H), 3.73 (d, *J* = 10 Hz, 1H), 6.22 (t, *J* = 7.3 Hz, 1H), 6.43 (t, *J* = 7.1 Hz, 1H). – ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 18.2 (q), 18.4 (q), 20.1 (t), 24.9 (t), 28.5 (d), 29.7 (t), 29.8 (d), 37.7 (d), 59.8 (s), 88.6 (d), 131.4 (d), 137.0 (d), 175.6 (s). – $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.79; found C 75.49, H 8.93.

endo-**2e**: M.p. 51–54°C. – IR (CCl_4): $\tilde{\nu}$ = 3050 cm^{-1}, 1820, 1710. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.01 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.21–1.41 (m, 2H), 1.43–1.60 (m, 2H), 1.64 (dt, *J* = 2.8 and 13.6 Hz, 1H), 1.76 (dd, *J* = 2.5 and 13.6, 1H), 1.90 (dsept, *J* = 6.6 and 9.8 Hz, 1H), 2.70 (br. s, 1H), 2.80 (br. s, 1H), 3.92 (d, *J* = 9.8 Hz, 1H), 6.32 (dt, *J* = 1.3 and 7.9 Hz, 1H), 6.45 (dt, *J* = 1.1 and 7.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 17.8 (q), 18.6 (q), 21.1 (t), 23.9 (t), 28.6 (t), 29.0 (d), 29.9 (d), 37.0 (d), 60.3 (s), 86.9 (d), 130.8 (d), 136.1 (d), 175.3 (s). – $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.79; found C 75.31, H 9.04.

Spiro-β-lactone **2f**: A suspension of **1** (200 mg, 1.58 mmol), anthracene (423 mg, 2.30 mmol), and a trace of hydroquinone (to inhibit radical polymerization) in 5 ml CH_2Cl_2 was heated at 130°C for 4.5 d in a sealed tube. The solvent was evaporated at reduced pressure (20°C/20 Torr), and the residue was purified by column chromatography [silica gel; petroleum ether/CH_2Cl_2 (1:1)]. Besides 72.0 mg of **1** (64% conversion), 204 mg (66%) of **2f** was obtained as colorless, amorphous solid. Crystals for the X-ray analysis were obtained by recrystallization from ether/pentane; m.p. 184–186°C. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 3040, 3020, 1830, 1730, 1710, 1690, 1680, 1660, 1640, 1630. – ^1H NMR ($CDCl_3$, 250 MHz): δ = –0.12 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 1.57 (dsept, *J* = 6.5 and 10.4 Hz, 1H), 2.00 (dd, *J* = 2.5 and 13.2 Hz, 1H), 2.06 (dd, *J* = 2.9 and 13.2 Hz, 1H), 3.84 (d, *J* = 10.4 Hz, 1H), 4.40 (t, *J* = 2.6 Hz, 1H), 4.49 (s, 1H), 7.07–7.40 (m, 8H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 15.3 (q), 18.5 (q), 29.2 (d), 32.1 (t), 43.4 (d), 51.4 (d), 60.7 (s), 87.2 (d), 123.0 (d), 124.0 (d), 124.5 (d), 125.4 (d), 126.2 (d), 126.3 (d), 126.8 (d), 127.0 (d), 138.0 (s), 139.5 (s), 143.1 (s), 143.2 (s), 173.4 (s). – $C_{21}H_{20}O_2$ (304.4): calcd. C 82.86, H 6.62; found C 82.58, H 6.46.

Table 5. Crystallographic data and refinement parameters of cycloadduct **2f**

Crystallographic section: $C_{21}H_{20}O_2$ (304.39); *a* = 1147.4(5), *b* = 1252.7(4), *c* = 1144.5(5) pm; β = 93.02(4)°; *V* = 1643(1) · 10^6 pm^3; *Z* = 4; *d*(calcd.) = 1.230 g · cm^{-3}; monoclinic; $P2_1/n$. – Data collection: Siemens R3m/V diffractometer; Mo-K_α radiation; graphite monochromator; crystal size 0.4 × 0.8 × 0.55 mm; Wyckoff scan; Θ = 1.75–27.5°; *h* = 0 → 14, *k* = 0 → 16, *l* = –14 → 14; number of reflections: 4113 measured, 3761 unique; 3303 with $F > 3\sigma(F)$; μ = 0.07 mm^{-1}; absorption correction: Ψ scan. – Structural analysis and refinement: Direct-phase determination; full-matrix least squares; hydrogen atom positions: riding model with fixed isotropic *U*; data-to-parameter ratio: 15.80; *R* = 0.049; R_w = 0.048, $w = 1/\sigma^2(F)$; largest difference peak: 0.30 $eÅ^{-3}$; largest difference hole: 0.21 $eÅ^{-3}$; Siemens SHELXTL PLUS program (Micro VAX II).

The details of the X-ray structure parameters for **2f** are shown in Table 5, and the coordinates are listed in Table 6. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56934, the names of the authors, and the journal citation.

Table 6. Atomic parameters [× 10^4] and equivalent isotropic displacement parameters [pm^2 × 10^{-1}] of cycloadduct **2f**

	x	y	z	U(eq)
C 1	15280(1)	13248(1)	12742(1)	41(1)
C 2	14010(1)	13317(1)	12167(1)	41(1)
C 3	13395(2)	14333(1)	12499(2)	48(1)
O 3	12970(1)	14706(1)	13337(1)	65(1)
O 4	13454(1)	14815(1)	11433(1)	58(1)
C 5	13997(2)	13847(1)	10936(1)	45(1)
C 6	15839(1)	12359(1)	12070(1)	41(1)
C 7	16780(2)	12462(1)	11365(2)	49(1)
C 8	17140(2)	11578(2)	10738(2)	56(1)
C 9	16566(2)	10615(2)	10814(2)	58(1)
C 10	15626(2)	10508(1)	11523(2)	51(1)
C 11	15266(1)	11379(1)	12155(1)	43(1)
C 12	14239(1)	11423(1)	12934(1)	45(1)
C 13	14664(1)	11889(1)	14100(1)	44(1)
C 14	14550(2)	11437(2)	15196(2)	53(1)
C 15	14949(2)	12005(2)	16184(2)	60(1)
C 16	15441(2)	13009(2)	16086(2)	57(1)
C 17	15571(2)	13461(2)	14991(1)	49(1)
C 18	15191(1)	12892(1)	14002(1)	42(1)
C 19	13370(1)	12256(1)	12376(2)	46(1)
C 50	13275(2)	13409(1)	9899(1)	50(1)
C 51	13092(2)	14281(2)	8971(2)	66(1)
C 52	13875(2)	12443(2)	9386(2)	71(1)

General Method for the Preparation of the Alkenes **3a–f**: The particular spiro-β-lactones **2a–f** (ca. 1–2 mmol) were placed into a flask connected to a quartz tube, which was equipped with a liquid N_2 trap. The quartz tube was heated to 400°C and the lactones **2a–f** were flash-distilled through the hot quartz tube by heating the β-lactone at 180°C/0.1 Torr. The products **3a–f** were collected in the cold trap and purified by preparative gas chromatography or, in the case of **3f**, by column chromatography. The purity of the alkenes **3a–f** was confirmed by gas chromatography. Yields are given in Table 3, and the details for the individual cases are described below.

(4E)-4-(2-Methylpropylidene)-1-cyclohexene (**3a**): According to the general procedure, by starting from 200 mg (1.10 mmol) of **2a**, there was obtained 150 mg (99%) of **3a** as colorless liquid, b.p. 20°C/0.1 Torr. – IR (CCl_4): $\tilde{\nu}$ = 3030 cm^{-1}, 1670, 1646. – ^1H NMR ($cDCl_3$, 250 MHz): δ = 0.95 (d, *J* = 6.7 Hz, 6H), 2.12 (m, 2H), 2.32 (t, *J* = 6.3 Hz, 2H), 2.60 (dsept, *J* = 6.6 and 9.0 Hz, 1H), 2.67 (m, 2H), 5.07 (d, *J* = 9.0 Hz, 1H), 5.67 (m, 2H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 23.6 (q), 25.5 (t), 26.1 (d), 27.4 (t), 35.3 (t), 126.8 (d), 127.2 (d), 130.2 (d), 133.1 (s). – $C_{10}H_{16}$ (136.2): calcd. C 88.16, H 11.83; found C 87.82, H 11.85.

(4E)-1-Methyl-4-(2-methylpropylidene)-1-cyclohexene (**3b**): According to the general procedure, by starting from 200 mg (1.03 mmol) of **2b**, there was obtained 142 mg (92%) of **3b** as colorless liquid, b.p. 20°C/0.1 Torr. – IR (CCl_4): $\tilde{\nu}$ = 3050 cm^{-1}, 3040, 3020, 1730, 1675. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.95 (d, *J* = 6.7 Hz, 6H), 1.65 (s, 3H), 2.03 (t, *J* = 5.5 Hz, 2H), 2.32 (t, *J* = 6.7 Hz, 2H), 2.60 (dsept, *J* = 6.6 and 9.2 Hz, 1H), 2.64 (m, 2H), 5.05 (d, *J* = 9.0 Hz, 1H), 5.36 (m, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 23.4 (q), 23.7 (q), 25.5 (t), 26.2 (d), 32.1 (t), 35.3 (t), 121.1 (d), 130.0 (d), 133.1

(s), 133.9 (s). – MS (70 eV): *m/z* (%) = 107 (100), 150 (88) [M^+]. – $C_{11}H_{18}$: calcd. 150.14085, found 150.14108 (MS).

(5E)-5-(2-Methylpropylidene)bicyclo[2.2.1]hept-2-ene (**3c**): According to the general procedure, by starting from 200 mg (1.04 mmol) of *exo-, endo-***2c**), there was obtained 105 mg (71%) of **3c** as colorless liquid, b.p. 20°C/0.1 Torr. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 1680, 1570, 1560. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.35 (d, *J* = 8.0 Hz, 1H), 1.5 (m, 1H), 1.7 (dt, *J* = 14.6 and 2.4 Hz, 1H), 2.15 (ddd, *J* = 2.5, 3.4 and 14.4 Hz, 1H), 2.24 (dsept, *J* = 6.7 and 9.0 Hz, 1H), 2.95 (br. s, 1H), 3.04 (br. s, 1H), 5.17 (dt, *J* = 2.5 and 9.0 Hz, 1H), 6.04 (dt, *J* = 3.6 and 5.4 Hz, 1H), 6.05 (dt, *J* = 2.9 and 5.4 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 22.8 (q), 23.1 (q), 29.3 (d), 30.7 (t), 41.8 (d), 50.1 (t), 50.5 (d), 126.6 (d), 134.6 (d), 135.8 (d), 138.7 (s). – $C_{11}H_{16}$ (148.2): calcd. C 89.12, H 10.87; found C 89.05, H 10.84.

(5E)-5-(2-Methylpropylidene)bicyclo[2.2.2]oct-2-ene (**3e**): According to the general procedure, by starting from 200 mg (0.97 mmol) of *exo-, endo-***2e**, there was obtained 118 mg (79%) of **3e** as colorless liquid, b.p. 20°C/0.1 Torr. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 1710, 1610, 1460. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.82 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 1.22–1.43 (m, 2H), 1.46–1.65 (m, 2H), 1.95 (dq, *J* = 2.7 and 16.1 Hz, 1H), 2.12 (dt, *J* = 2.4 and 16.1 Hz, 1H), 2.28 (dsept, *J* = 6.6 and 9.1 Hz, 1H), 2.67 (br. s, 1H), 2.86 (m, 1H), 4.90 (dt, *J* = 2.4 and 9.1 Hz, 1H), 6.24 (dq, *J* = 1.6 and 8.1 Hz, 1H), 6.27 (dq, *J* = 1.7 and 8.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 22.6 (q), 22.9 (q), 25.3 (t), 26.8 (t), 27.4 (d), 31.3 (d), 32.1 (t), 41.0 (d), 127.1 (d), 133.5 (d), 133.6 (d), 138.0 (s). – $C_{12}H_{18}$ (162.3): calcd. C 88.82, H 11.18; found C 88.81, H 11.22.

(11E)-9,10-Dihydro-11-(2-methylpropylidene)-9,10-ethanoanthracene (**3f**): According to the general procedure, by starting from 200 mg (0.66 mmol) of **2f**, there was obtained 161 mg (94%) of **3f** after column chromatography (silica gel; petroleum ether) as colorless, amorphous solid; m.p. 99–102°C. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 3040, 3020, 1935, 1900, 1860, 1830, 1810, 1790, 1670, 1625, 1480, 1465, 1455. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.82 (d, *J* = 6.6 Hz, 6H), 2.16 (dsept, *J* = 6.6 and 9.1 Hz, 1H), 2.35 (t, *J* = 2.5 Hz, 2H), 4.39 (t, *J* = 2.6 Hz, 1H), 4.58 (s, 1H), 5.31 (dt, *J* = 2.2 and 9.2 Hz, 1H), 7.07 (m, 4H), 7.26 (m, 4H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 22.5 (q), 28.1 (d), 32.2 (t), 44.8 (d), 55.3 (d), 123.1 (d), 123.2 (d), 125.5 (d), 125.7 (d), 129.9 (d), 134.4 (s), 142.9 (s), 143.2 (s). – $C_{20}H_{20}$ (260.4): calcd. C 92.25, H 7.75; found C 92.03, H 7.94.

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