Articles

Versatile Synthesis of 11-Oxabicyclo[4.4.1]undeca-1,5-dienes by Selective Epoxidation of 1,6-Disubstituted (*E,Z,E*)-1,3,5-Hexatrienes and Subsequent Cope Rearrangement

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1,6-Disubstituted (*E,Z,E*)-1,3,5-hexatrienes (**1a**−**c**, **2a**−**e**), obtained in good yields (43−81%) by 2-fold Heck couplings of 1,2-dibromocyclopentene and 1,2-dibromocyclohexene, respectively, with alkenes, can be oxidized regioselectively at the central double bond with various oxidants such as dimethyldioxirane (DMDO), *m*-CPBA, or trifluoroperacetic acid in moderate to good yields (45−87%). The resulting 1,2-dialkenylcyclohexene epoxides **4a**−**e** undergo thermal Cope rearrangements to furnish 1,6-oxygen-bridged cyclodeca-1,5-dienes **8a**−**e**, which are 2-fold anti-Bredt bridgehead alkenes. The structure of compound **8a** was established by X-ray analysis. The corresponding 1,2-dialkenylcyclopentene epoxides **3a**−**c** give only 2,2-dialkenylcyclopentanones **9a,b** by an acid-catalyzed 1,2-alkenyl shift (71−100% yield) or indan derivatives **12b,c** (46−82%) resulting from elimination, 6π-electrocyclization, and aromatization.

Introduction

The palladium-catalyzed alkenylations of alkenyl and aryl halides often proceed in excellent yields, even when performed with oligohalogen derivatives.[1,2] Vicinal dibromoalkenes and dibromocycloalkenes under conditions close to those originally reported by Heck[3] gave good yields of 1,6-disubstituted (*E,Z,E*)-1,3,5-hexatrienes that are versatile intermediates for further elaboration.[2] It appeared to us that a potentially useful transformation of these (*E,Z,E*)-1,3,5-hexatrienes would be the selective epoxidation[4] of their central tetrasubstituted double bond as it would lead to bridged 1,2-dialkenyloxiranes.

These epoxides would be perfectly set up for Cope rearrangements,[5] which ought to yield 1,6-oxygen-bridged cycloalka-1,5-dienes of the same type that Rastetter et

al. have previously prepared along a more tedious and less flexible route.[6] The carbocyclic analogues of such so-called anti-Bredt[7,8] bridgehead dienes, bicyclo[4.3.1]deca-1,5-diene and bicyclo[4.4.1]undeca-1,5-diene, have in fact been obtained by Shea et al., applying Cope rearrangements of 1,5-diethenylbicyclo[3.1.0]hexane and 1,6-diethenylbicyclo[4.1.0]heptane, respectively.[9] On the other hand, Cope rearrangements of simple *cis*-1,2-dialkenyloxiranes have been shown to lead to 4,5-dihydrooxepines,[10] which are found as fragments of a number of

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Scheme 1[a]

	R
a	Ph
b	CO_2Me
c	CO_2tertBu
d	CO_2Menthyl
e	CO_2-8-Phenylmenthyl
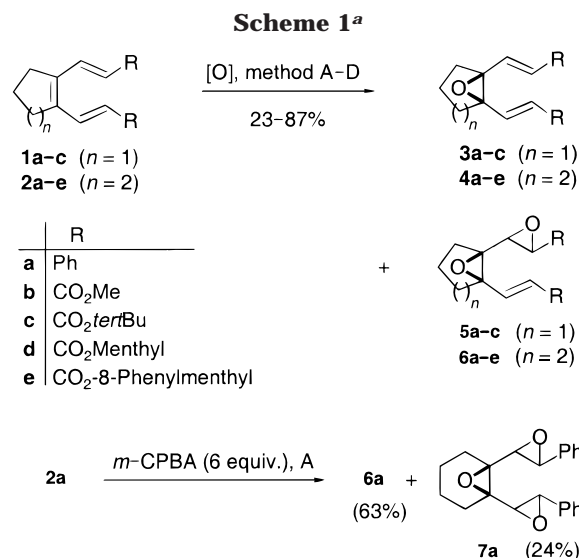
[a] Key: (A) *m*-CPBA, Et_2O, 20 °C; (B) *m*-CPBA, CH_2Cl_2, Na_2HPO_4, 20 °C; (C) DMDO, acetone, $-20 \rightarrow 20$ °C; (D) CF_3CO_3H, CH_2Cl_2, Na_2HPO_4, 40 °C.

Table 1. Epoxidation of 1,3,5-(*E,Z,E*)-Hexatrienes 1a−c and 2a−e

| entry	hexatriene	oxidant (equiv)	time (h)/ T (°C)	product	yield[a] (%)
1	**1a**	*m*-CPBA (2)	$15/0 \rightarrow 20$	**3a**	84
2	**2a**	*m*-CPBA (2)	$15/0 \rightarrow 20$	**4a**	87
3	**2a**	*m*-CPBA (6)	$15/0 \rightarrow 20$	**6a + 7a**	$63^b + 24^c$
4	**2b**	*m*-CPBA (2)	$24/0 \rightarrow 20$	**4b**	34
5	**1c**	*m*-CPBA (2)	$24/0 \rightarrow 20$	**3c**	82
6	**2c**	*m*-CPBA (2)	$24/0 \rightarrow 20$	**4c**	74
7	**2d**	*m*-CPBA (2)	$24/0 \rightarrow 20$	**4d**	23
8	**1a**	DMDO (1.6)	$16/-20 \rightarrow 20$	**3a**	66
9	**2a**	DMDO (1.9)	$7/-20 \rightarrow 20$	**4a**	73
10	**1b**	DMDO (3.8)	$50/-20 \rightarrow 20$	**3b**	64
11	**2c**	DMDO (3.2)	$44/-20 \rightarrow 20$	**4c**	44
12	**2b**	CF_3CO_3H (10)	1/40	**4b**	64
13	**2c**	CF_3CO_3H (7)	1/40	**4c**	74
14	**2d**	CF_3CO_3H (9)	1/40	**4d**	45
15	**2e**	CF_3CO_3H (5)	1/40	**4e**	63

[a] Isolated yield after CC on aluminum oxide (activity II−III). [b] Isolated as a mixture of two diastereomers (3:1). [c] Isolated as a mixture of three diastereomers (1:0.7:0.2).

biologically active natural products,[11] and much effort has been spent on the analysis of the benzene oxide−oxepine equilibrium.[12] In order for these [3,3]-sigmatropic rearrangements to occur, it is essential that the two alkenyl substituents on the oxirane ring are cis with respect to each other, as the *trans*-1,2-dialkenyloxiranes are stable under the conditions that led to rearrangement of the cis isomers.[10b,c,f]

Results and Discussion

The epoxidation of hexatrienes **1** and **2** was first performed with *m*-CPBA[13] to give the epoxides **3** and **4** in moderate to good yields (Scheme 1, Table 1, entries 1−7). Unfortunately, though, small amounts of starting mate-

Scheme 2[a]

	R
a	Ph
b	CO_2Me
c	CO_2tertBu
d	CO_2Menthyl
e	CO_2-8-Phenyl-menthyl
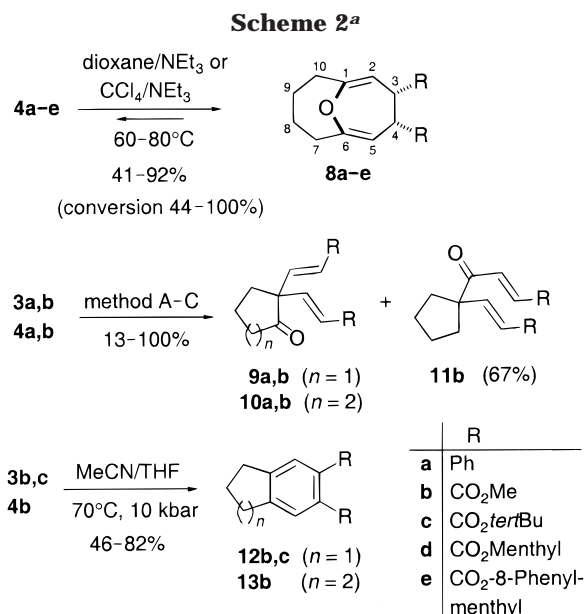
[a] Key: (A) toluene-d_8, 110 °C, 1 bar; (B) CH_2Cl_2, 20 °C, 12 kbar; (C) $BF_3 \cdot OEt_2$, Et_2O, 20 °C, 1 bar.

rials **1** and **2** as well as bisepoxides **5** and **6** were isolated in all cases. With a large excess of *m*-CPBA, only the bis- and trisepoxides **6a** and **7a** were formed (Table 1, entry 3). Because the results were highly dependent on the quality and source of the *m*-CPBA, other oxidizing reagents were screened. For the phenyl-substituted hexatrienes **1a** and **2a**, dimethyldioxirane[14] was found to be almost as efficient as *m*-CPBA (Table 1, entries 8 and 9). For the alkoxycarbonyl-substituted compounds **2b,c**, trifluoroperacetic acid, prepared from trifluoroacetic acid anhydride and the H_2O_2−urea complex,[15] worked best. Consistently good yields were thus achieved, and only small amounts of di- and triepoxides were formed (Table 1, entries 12−15). The epoxides **3** and **4** in general are colorless solids and are sensitive toward acids and heat but can easily be purified by column chromatography on aluminum oxide and/or recrystallization. Thus, with the differently substituted double bonds present in the 1,3,5-hexatrienes **1** and **2**, the epoxidation regioselectively occurs at the most nucleophilic one and therefore is influenced by the substituents on the 1- and 6-positions.

Different conditions for the thermal Cope rearrangement of the epoxides **3a−c** and **4a−e** were tested. Upon heating a solution of **4a** in CCl_4/NEt_3 (1:1) at 80 °C, the bridgehead diene *endo,endo*-3,4-diphenyl-11-oxabicyclo-[4.4.1]undeca-1,5-diene (**8a**) was obtained as the sole product, but the conversion of **4a** to **8a** did not go beyond 60% (Scheme 2, Table 2, entry 5), as apparently the Cope rearrangement of **4a** is reversible. In fact, when isolated **8a** was subjected to the same conditions, a 40:60 mixture of **4a** and **8a** was also observed. This ratio hardly depends on the nature of the solvent (Table 2, entry 6). Heating

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Table 2. Rearrangements of the Dialkenylepoxides 3 and 4

| entry	epoxide	solvent	T (°C)/time (h)/pressure (bar)	product	yield[a] (%)
1	3a	CCl$_4$/NEt$_3$	100/15/1	9a	0[b]
2	3a	CH$_2$Cl$_2$	20/14/1.2 × 10^4	9a	quant
3	3a	toluene-d_8[c]	110/8/1	9a	75
4	3a	Et$_2$O[d]	20/0.08/1	9a	96
5	4a	CCl$_4$/NEt$_3$	80/15/1	8a	48[b]
6	4a	dioxane	80/23/1	8a	41[b]
7	4a	toluene-d_8[c]	110/5/1	10a	65
8	4a	Et$_2$O[d]	20/0.08/1	10a	91
9	3b	dioxane	80/15/1	9b	0[b]
10	3b	BF$_3$·OEt$_2$	25/0.5/1	9b	71
11	3b	MeCN/THF	70/72/10^4	12b	82
12	4b	dioxane	60/22/1	8b	92
13	4b	BF$_3$·OEt$_2$	25/0.17/1	10b	13[e]
14	4b	THF	70/50/10^4	13b	72
15	3c	dioxane	80/21/1	9c	0[b]
16	3c	MeCN/THF	20/24/10^4	12c	0[b]
17	3c	MeCN/THF	70/72/10^4	12c	46[b]
18	4c	dioxane	80/19/1	8c	83
19	4c	CCl$_4$/NEt$_3$	80/22/1	8c	69
20	4d	dioxane	80/17/1	8d	88
21	4e	dioxane	80/17/1	8e	83

[a] Isolated yield. [b] Unreacted starting material was also isolated. [c] No base added. [d] BF$_3$·OEt$_2$ was added. [e] Plus 67% of **11b**.

of the epoxides **4b−e** in dioxane led to the analogous 3,4-bis(alkoxycarbonyl)-substituted bridgehead dienes in even better yields, as complete conversions were achieved (Table 2, entries 12, 18, 20 and 21).

Recrystallization of the diphenyl derivative **8a** from hexane furnished crystals suitable for an X-ray structure analysis, which rigorously proved the structure of the bridgehead diene as a 3,4-bis-endo configuration (Figure 1).[16] The C^1−C^2 and C^5−C^6 distances (1.324 and 1.325 Å, respectively) are normal for a carbon−carbon double bond (e.g., C=C in ethylene: 1.332 Å), but the bond angles are exceptional as the bridgehead carbons are significantly pyramidalized, and the double bonds are twisted. The geometrical constraints at the bridgehead carbon atoms (C^1 and C^6) open up the angles C^{10}−C^1−C^2 to 128.0° and C^7−C^6−C^5 to 131.0° and decrease the angles C^{10}−C^1−O,^{11} O^{11}−C^6−C^5, and C^7−C^6−O^{11} to 111.0°, 116.4°, and 112.2°, respectively. The X-ray crystal structure of the 1,6-oxygen-bridged 1,5-nonadiene derivative previously reported by Rastetter et al.[6b] revealed similar bond angles for the bridgehead carbon atoms. For example, the bond angles around C^6 of the 10-oxabicyclo-[4.3.1]deca-1,5-diene derivative are 132.0° (**8a** 131.0°), 115.8° (**8a** 116.4°), and 109.7° (**8a** 112.2°). However, the torsional angles around the double bonds are expectedly larger in the 10-oxabicyclo[4.3.1]deca-1,5-diene derivative than in **8a** (5.5° and 17.7° vs 1.5° and 9.9°, see Figure 1).

By analogy, the NMR spectra of **8b−e** corroborate corresponding structures with a bis-endo orientation of the two alkoxycarbonyl substituents. Apparently, the [3,3]-sigmatropic rearrangements of all five 1,2-dialkenyl epoxides **4a−e** proceed via boatlike transition structures. In general, a Cope rearrangement of a 1,n-dialkenylbicyclo[n-2.1.0]alkane can proceed via a chairlike or two boatlike transition structures. The chairlike transition structure leads to cycloalkadiene derivatives with an E,Z configuration and an endo,endo-oriented boatlike transition structure—with respect to the main bridge—leads to
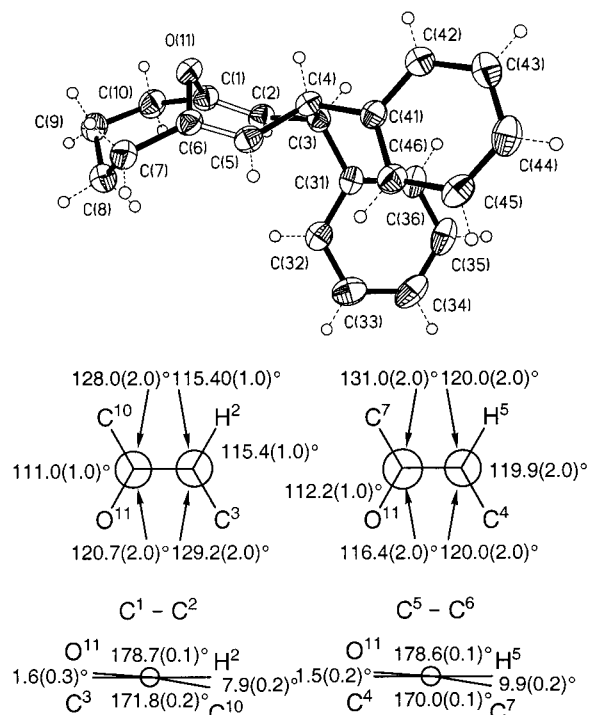
Figure 1. ORTEP drawing and bond and torsional angles around the double bonds of compound **8a**.

a bridged (Z,Z)-1,5-cycloalkadiene, whereas the exo,exo-oriented one ends up as an E,E-configurated derivative. In small and medium 1,5-cycloalkadienes the Z,Z isomers are most stable,[17] and therefore, the formation of oxepines **8** in which the double bonds have a Z,Z configuration with respect to the 7-membered ring and an E,E configuration in the 10-membered ring is the expected result.

Upon heating the five-membered-ring derivatives **3a−c**, no Cope-rearrangement products could be detected (Table 2, entries 1, 9, and 15). The diphenyl derivative **3a**, even when heated at 100 °C for 15 h, gave only unchanged starting material. Subjecting dimethoxycarbonyl epoxide **3b** to flash vacuum pyrolysis at temperatures ranging from 400 to 650 °C at a pressure of 10^{-5} bar also did not lead to the formation of the oxepine, only the starting material **3b**, the corresponding epoxide with an E- and a Z-configured double bond, and a large number of unidentified products were obtained. In contrast, 1,5-diethenylbicyclo[3.1.0]hexane, formed by Wittig olefination of the corresponding bridgehead dialdehyde, could not be observed as it immediately rearranged to the bridgehead diene as an oxygen-sensitive but isolable substance.[9] As application of high pressure is expected to cause a rate enhancement in Cope rearrangements,[18a] a solution of **3c** in THF/MeCN was subjected to a pressure of 10 kbar for 24 h, but only starting material was recovered (Table 2, entry 16). When exposing the distyryl epoxide **3a** as a solution in CH$_2$Cl$_2$ to high pressure, 2,2-distyrylcyclopentanone (**9a**) was formed. This rearrangement of **3a** apparently occurs by a 1,2-alkenyl shift most probably as a consequence of the

(16) The authors have deposited atomic coordinates for **8a** with the Cambridge Crystallographic Data Centre as no. CCDC-115082. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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increased polarity of CH_2Cl_2 under high pressure (entry 2).[18b] With traces of acid added to a solution of **3a** at room temperature (e.g., $BF_3 \cdot OEt_2$), the cyclopentanone **9a** was formed rapidly and cleanly as well (Table 2, entry 4). The homologous epoxide **4a** also undergoes this 1,2-styryl shift under acidic conditions (Table 2, entries 7 and 8). Such acid-catalyzed rearrangements have previously been observed for other 1,2-dialkenyloxiranes.[6a,19]

For rearrangements of the alkoxycarbonyl-substituted epoxides **3b** and **4b** it was necessary to run the reactions in pure $BF_3 \cdot OEt_2$. In the case of **3b**, the expected cyclopentanone **9b** was formed while **11b**, the product of an alkyl chain shift, was the main product in rearrangement of epoxide **4b** (Table 2, entries 10, 13). Upon heating the epoxides to 70 °C in THF or THF/MeCN under high pressure, the indan derivatives **12b,c** and the tetrahydronaphthalene derivative **13b** were formed in good to very good yields (Table 2, entries 11, 14, and 17). The mechanism of this transformation is not yet understood, but formally deoxygenation of the epoxide to reform the double bond, 6π-electrocyclization, and aromatization would lead to this type of product. Altogether this process is a dehydration reaction that is probably favored under high-pressure conditions because of the so-called electrostriction effect: generally, reactions show a negative reaction volume if covalent molecules (e.g., the water molecules) dissociate to form ions.[18c] This effect and the formation of the aromatic systems should be the driving forces for this unexpected reaction.

Conclusion

The sequence of selective epoxidation and Cope rearrangement of (E,Z,E)-1,3,5-hexatrienes, prepared by 2-fold Heck coupling of dibromocyclohexene, is an attractive fast and flexible route to oxygen-bridged bridgehead cyclodecadienes **8**. As the latter are formed reversibly under equilibrating conditions, the differences in energy between bridged dialkenyl epoxides and their isomeric oxepines are decisive for the equilibrium composition. While epoxide **4a** and bridgehead diene **8a** with phenyl substituents apparently are of nearly the same energy, alkoxycarbonyl-substituted cyclodecadienes **8b–e** are more stable than the corresponding dialkenyl epoxides. Obviously, a significant increase in strain does occur on going from the 1,6-oxygen-bridged 1,5-cyclodecadiene to the lower homologue just as was calculated for the carbocyclic analogues with a difference of 7 kcal/mol in steric energy between bicyclo[4.3.1]deca-1,5-diene and bicyclo[4.4.1]undeca-1,5-diene.[8,9b] The 1,2-dialkenylcyclopentene epoxide **3** does not undergo the Cope rearrangement, although its carbon analogue, the 1,5-diethenylbicyclo[3.1.0]hexane, rearranges even faster than the homologous 1,6-diethenylbicyclo[4.1.0]heptane.[9a] This difference must be attributed to a significant difference in the respective activation energies of a 1,2-diethenylcyclopropane and 2,3-diethenyloxirane, as *cis*-1,2-diethenylcyclopropane rearranges at 5 °C to form 1,4-cycloheptadiene ($\Delta H^{\ddagger} = 19.4$ kcal/mol, $\Delta S^{\ddagger} = -5.30$ cal/K mol)[20] while a temperature of 100 °C is necessary for the rearrangement of *cis*-2,3-diethenyloxirane ($\Delta H^{\ddagger} = 24.6$ kcal/mol, $\Delta S^{\ddagger} = -11.3$ cal/K mol).[10e,12a]

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Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded in CDCl$_3$ solution at 200, 250, or 500 MHz and 50.3 or 62.9 MHz, respectively. Chemical shifts are reported in δ (ppm) relative to the CHCl$_3$ signal, recalculated relative to tetramethylsilane (TMS). MS was performed with an ionizing voltage of 70 eV. HRMS used a preselected ion peak matching at $R \gg 10000$ to be within $\pm$ 2 ppm of the exact masses. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were technical grade and distilled before use. Flash chromatography was performed using Merck Kieselgel 60 (200–400 mesh). Aluminum oxide (ICN Alumina N–Super I) was obtained from ICN BIOMEDICALS. The rearrangement reactions were carried out under an atmosphere of dry nitrogen or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solutions of NH$_4$Cl, NaCl, and NaHCO$_3$ are saturated aqueous solutions. Tetrahydrofuran, dioxane, and diethyl ether were distilled from potassium benzophenone ketyl, and CH$_2$Cl$_2$, NEt$_3$, and MeCN were distilled from CaH$_2$. Hexatrienes **1a–c** and **2a–e** were prepared according to ref 2a,b, and DMDO was prepared according to ref 14e.

General Procedure for the Epoxidation of 1,2-Distyrylcycloalkenes 1a and 2a with *m*-CPBA (GP 1). To a solution of the 1,3,5-(E,Z,E)-hexatriene (0.1 mmol) in Et$_2$O (5 mL) at 0 °C was added a solution of *m*-CPBA (70%) (49 mg, 0.2 mmol) in Et$_2$O (5 mL). The reaction mixture was stirred for 15 h at 20 °C, diluted with Et$_2$O (50 mL), washed with Na$_2$SO$_3$ (20 mL, 10%), NaHCO$_3$ (2 × 20 mL), and NaCl (20 mL), dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was chromatographed on neutral aluminum oxide (activity III).

1,5-(E,E)-Distyryl-6-oxabicyclo[3.1.0]hexane (3a). 1,2-(E,E)-Distyrylcyclopentene (**1a**) (200 mg, 0.73 mmol) was epoxidized according to GP 1. Column chromatography (CC) on aluminum oxide (petroleum ether/Et$_2$O 10:1, column 2 × 20 cm) yielded 177 mg (84%) of **3a** as colorless plates: mp 129 °C; R_f = 0.15; ^1H NMR δ 1.65 (m$_c$, 2 H), 2.13 (m$_c$, 4 H), 6.24 (d, J = 16.2 Hz, 2 H), 6.78 (d, J = 16.2 Hz, 2 H), 7.22–7.47 (m, 10 H); ^{13}C NMR δ 18.65, 30.13, 72.92, 124.95, 126.40, 127.77, 128.55, 133.07, 136.49; MS m/z 288 (100) [M$^+$]. Anal. Calcd for C$_{21}$H$_{20}$O (288.4): C, 87.46; H, 6.99. Found: C, 87.00; H, 6.92.

1,6-(E,E)-Distyryl-7-oxabicyclo[4.1.0]heptane (4a). 1,2-(E,E)-Distyrylcyclohexene (**2a**) (50 mg, 0.18 mmol) was epoxidized according to GP 1. CC on aluminum oxide (petroleum ether/CH$_2$Cl$_2$ 4:1, column 1 × 20 cm) yielded 46 mg (87%) of **4a** as colorless crystals: mp 142 °C; R_f = 0.33; ^1H NMR δ 1.35–1.50 (m, 2 H), 1.52–1.71 (m, 2 H), 2.11 (m$_c$, 4 H), 6.32 (d, J = 16.2 Hz, 2 H), 6.67 (d, J = 16.2 Hz, 2 H), 7.17–7.46 (m, 10 H); ^{13}C NMR δ 20.30, 28.57, 66.33, 126.43, 127.59, 128.55, 129.17, 132.16, 136.84; MS m/z 302 (68) [M$^+$]. Anal. Calcd for C$_{22}$H$_{22}$O (302.4): C, 87.38; H, 7.33. Found: C, 87.28; H, 7.42.

1-[1′,2′-Epoxy-(E)-styryl]-6-(E)-styryl-7-oxabicyclo[4.1.0]heptane (6a) and 1,6-(E,E)-Di(1′,2′-epoxystyryl)-7-oxabicyclo[4.1.0]heptane (7a). According to GP 1, 1,2-(E,E)-distyrylcyclohexene (**2a**) (50 mg, 0.18 mmol) was reacted with *m*-CPBA (259 mg, 1.05 mmol) for 15 h. CC on aluminum oxide (petroleum ether/Et$_2$O 10:1, column 1 × 20 cm) afforded 35 mg (63%) of **6a** (R_f = 0.2) as a mixture of two diastereomers (3:1); the major one can be obtained up to 94% pure after two recrystallizations from hexane: mp 112 °C; ^1H NMR δ 1.29–1.67 (m, 4 H), 1.92–2.08 (m, 4 H), 3.08 (d, J = 2.1 Hz, 1 H), 4.01 (d, J = 2.1 Hz, 1 H), 6.26 (d, J = 16.1 Hz, 1 H), 6.67 (d, J = 16.1 Hz, 1 H), 7.13–7.29 (m, 10 H); ^{13}C NMR δ 19.70, 19.99, 24.14, 28.82, 56.15, 63.14, 63.80, 64.74, 125.58, 126.39, 127.59, 127.78, 128.11, 128.34, 128.51, 132.35, 136.25, 136.56. Anal. Calcd for C$_{22}$H$_{22}$O$_2$ (318.4): C, 82.99; H, 6.96. Found: C, 82.88; H, 7.00. From fraction II (R_f = 0.14), 14 mg (24%) of **7a** as colorless crystals after recrystallization from hexane was obtained as a mixture of three diastereomers (1:0.7:0.2), mp 130 °C. Diastereomer I: ^1H NMR δ 1.25–1.62 (m, 4 H), 1.79–2.05 (m, 4 H), 3.18 (d, J = 2.1 Hz, 1 H), 3.26 (d, J = 2.1 Hz, 1 H), 3.78 (d, J = 2.1 Hz, 1 H), 4.02 (d, J = 2.1 Hz, 1

H), 7.03−7.29 (m, 10 H); ^{13}C NMR δ 19.53, 24.18, 24.21, 55.06, 56.17, 61.12, 62.47, 62.71, 125.49, 128.32, 128.46, 128.47, 136.24, 136.30. Diastereomer II: ^{1}H NMR δ 1.25−1.62 (m, 4 H), 1.79−2.05 (m, 4 H), 3.16 (d, J = 2.0 Hz, 2 H), 3.93 (d, J = 2.0 Hz, 2 H), 7.03−7.29 (m, 10 H); ^{13}C NMR δ 19.60, 24.56, 52.93, 62.50, 62.67, 125.65, 128.28, 128.47, 136.20. Diastereomer III: ^{1}H NMR δ 1.25−1.62 (m, 4 H), 1.79−2.05 (m, 4 H), 3.22 (d, J = 2.1 Hz, 2 H), 3.76 (d, J = 2.1 Hz, 2 H), 7.03−7.29 (m, 10 H); ^{13}C NMR δ 19.50, 23.88, 55.52, 61.48, 62.88, 125.52, 128.09, 128.36, 136.37; MS m/z 334 (1) [M$^+$]. Anal. Calcd for C$_{22}$H$_{22}$O$_3$ (334.4): C, 79.02; H, 6.63. Found: C, 79.00; H, 6.65.

General Procedure for the Epoxidation of 1,2-Distyryl-cycloalkenes 1a and 2a and the Diesters 1b and 2c with DMDO (GP 2). To a solution of the (*E*,*Z*,*E*)-1,3,5-hexatriene (0.5 mmol) in acetone (20 mL) at −20 °C was added a precooled (−78 °C) solution of DMDO in acetone (5 mL, 0.1 m). The reaction mixture was slowly warmed to 20 °C, stirred at this temperature, and monitored by TLC. If starting material was detected after 12 h of stirring, the mixture was cooled again and a solution of DMDO (5 mL, 0.1 m) was added again. At the end of the reaction, the acetone was evaporated in vacuo, and the residue was chromatographed on neutral aluminum oxide (activity III).

Methyl 3-(*E*)-[5-[2-(*E*)-Methoxycarbonylethenyl]-6-oxabicyclo[3.1.0]hex-1-yl]acrylate (3b). The dimethyl ester **1b** (100 mg, 0.42 mmol) was reacted with DMDO (4 × 4 mL, 1.60 mmol) according to GP 2 for 50 h. The residue was chromatographed on aluminum oxide (petroleum ether/EtOAc 4:1, column 20 × 1 cm). Fraction I (R_f = 0.31): 20 mg (20%) of the starting material **1b**. Fraction II (R_f = 0.25): 68 mg (64%) of **3b** as a colorless oil: IR (cm^{-1}, film) 1720; ^{1}H NMR δ 1.42−1.79 (m, 2 H), 1.92−2.19 (m, 4 H), 3.69 (s, 6 H), 6.11 (d, J = 15.8 Hz, 2 H), 6.83 (d, J = 15.8 Hz, 2 H); ^{13}C NMR δ 18.72, 29.94, 51.77, 72.64, 123.93, 141.72, 165.99; MS m/z 252 (5) [M$^+$]. Anal. Calcd for C$_{13}$H$_{16}$O$_5$: 252.0998 (correct mass according to HRMS).

General Procedure for the Epoxidation of (*E*,*Z*,*E*)-1,3,5-Hexatriene-1,6-dicarboxylates (GP 3) with *m*-CPBA. To a solution of the hexatriene (1.00 mmol) in CH$_2$Cl$_2$ (30 mL) at 0 °C were added *m*-CPBA (70%) (493 mg, 2.00 mmol) and Na$_2$HPO$_4$·2H$_2$O (712 mg, 4.00 mmol). The mixture was stirred for 24 h at rt. When the reaction had ceased, the mixture was diluted with CH$_2$Cl$_2$ (30 mL), washed with Na$_2$SO$_3$ (20 mL, 10%), NaHCO$_3$ (2 × 20 mL), and NaCl (20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was chromatographed on neutral aluminum oxide (activity II, petroleum ether/EtOAc) and recrystallized from hexane.

***tert*-Butyl 3-(*E*)-[5-[2-(*E*)-*tert*-Butoxycarbonylethenyl]-6-oxabicyclo[3.1.0]hex-1-yl]acrylate (3c).** The hexatriene **1c** (700 mg, 2.18 mmol) was reacted according to GP 3. CC on aluminum oxide (petroleum ether/EtOAc 40:1, column 2.5 × 20 cm) furnished 600 mg (82%) of the epoxide **3c** (R_f = 0.25) as a colorless powder: mp 62 °C; IR (cm^{-1}, KBr): 1705; ^{1}H NMR δ 1.47 (s, 18 H), 1.61−1.77 (m, 2 H), 1.89−2.18 (m, 4 H), 6.02 (d, J = 15.7 Hz, 2 H), 6.71 (d, J = 15.7 Hz, 2 H); ^{13}C NMR δ 18.59, 28.04, 29.84, 72.40, 80.78, 126.16, 140.51, 164.90. Anal. Calcd for C$_{19}$H$_{28}$O$_5$ (336.4): C, 67.83; H, 8.39. Found: C, 67.89; H, 8.43.

General Procedure for the Epoxidation of (*E*,*Z*,*E*)-1,3,5-Hexatriene-1,6-dicarboxylates with Trifluoroperacetic Acid (GP 4). To a suspension of hydrogen peroxide−urea complex (395 mg, 4.20 mmol) in anhydrous MeCN (4 mL) was added a solution of trifluoroacetic acid anhydride (735 mg, 3.50 mmol) in anhydrous MeCN (2 mL) at 0 °C within 5 min. The mixture was stirred for an additional 45 min at this temperature. A suspension of the hexatriene **2** (0.500 mmol) and Na$_2$HPO$_4$·2H$_2$O (1.25 g, 7.00 mmol) in anhydrous CH$_2$Cl$_2$ (15 mL) was heated under reflux. Under vigorous stirring, the solution of the trifluoroperacetic acid was added over a period of 30 min. The whole reaction mixture was then stirred for an additional 30 min at 40 °C and, after cooling to rt, diluted with CH$_2$Cl$_2$ (30 mL), washed with Na$_2$SO$_3$ (20 mL, 10%), NaHCO$_3$ (2 × 20 mL), and NaCl (20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was chromatographed on neutral aluminum oxide (activity II).

Methyl 3-(*E*)-[6-[2-(*E*)-Methoxycarbonylethenyl]-7-oxabicyclo[4.1.0]hept-1-yl]acrylate (4b). Hexatriene **2b** (150 mg, 0.599 mmol) was reacted according to GP 4 with CF$_3$-CO$_3$H (10 equiv, 6.0 mmol). CC on aluminum oxide (petroleum ether/EtOAc 10:1, column 3 × 15 cm) yielded 13 mg (9%) of the starting material **2b** and 102 mg (64%) of the epoxide **4b** (R_f = 0.28) as a colorless powder: mp 62 °C; IR (cm^{-1}, KBr): 1726; ^{1}H NMR δ 1.34−1.45 (m, 2 H), 1.50−1.63 (m, 2 H), 1.99 (m$_c$, 4 H), 3.73 (s, 6 H), 5.99 (d, J = 15.7 Hz, 2 H), 6.77 (d, J = 15.7 Hz, 2 H); ^{13}C NMR δ 19.51, 27.68, 51.70, 65.60, 123.29, 145.17, 167.03; MS m/z 266 (13) [M$^+$]. Anal. Calcd for C$_{14}$H$_{18}$O$_5$ (266.3): C, 63.15; H, 6.81. Found: C, 63.25; H, 6.75.

***tert*-Butyl 3-(*E*)-[6-[2-(*E*)-*tert*-Butoxycarbonylethenyl]-7-oxabicyclo[4.1.0]hept-1-yl]acrylate (4c).** Hexatriene **2c** (100 mg, 0.299 mmol) was reacted according to GP 4 with CF$_3$-CO$_3$H (7.0 equiv, 2.1 mmol). CC on aluminum oxide (petroleum ether/EtOAc 25:1, column 3 × 15 cm) afforded 77 mg (74%) of the epoxide **4c** (R_f = 0.47) as a colorless powder, mp 82 °C, and 21 mg of more highly oxidized products: IR (cm^{-1}, KBr): 1712; ^{1}H NMR δ 1.49 (s, 18 H), 1.50−1.61 (m, 4 H), 1.96−2.08 (m, 4 H), 5.92 (d, J = 15.7 Hz, 2 H), 6.67 (d, J = 15.7 Hz, 2 H); ^{13}C NMR δ 19.60, 27.87, 28.15, 65.44, 80.58, 125.46, 144.03, 165.12. Anal. Calcd for C$_{20}$H$_{30}$O$_5$ (350.5): C, 68.55; H, 8.63. Found: C, 68.48; H, 8.65.

(1*R*,2*S*,5*R*)-Menthyl 3-(*E*)-[6-[2-(*E*)-(1*R*,2*S*,5*R*)-Menthoxy-carbonylethenyl]-7-oxabicyclo[4.1.0]hept-1-yl]acrylate (4d). Hexatriene **2d** (249 mg, 0.499 mmol) was reacted according to GP 4 with CF$_3$CO$_3$H (9.0 equiv, 4.5 mmol) and afforded after CC on aluminum oxide [petroleum ether/EtOAc 35:1 (150 mL), then petroleum ether/EtOAc 25:1 (400 mL), then petroleum ether/EtOAc 10:1, column 3 × 14 cm] 27 mg (11%) of the starting material **2d**, 115 mg (45%) of the epoxide **4d** (R_f = 0.15, petroleum ether/EtOAc 35:1), and 44 mg of more highly oxidized products: [α]$^{20}_D$ = −76.3 (c 1.00, CHCl$_3$); IR (cm^{-1}, KBr) 1717; ^{1}H NMR δ 0.73 (d, J = 6.9 Hz, 6 H), 0.84−1.12 (m, 6 H), 0.87 (d, J = 7.0 Hz, 6 H), 0.88 (d, J = 6.4 Hz, 6 H), 1.34−1.60 (m, 8 H), 1.63−1.69 (m, 4 H), 1.76−1.90 (m, 2 H), 1.97−2.10 (m, 4 H), 4.71 (m$_c$, 2 H), 5.98 (d, J = 15.7 Hz, 1 H), 5.98 (d, J = 15.7 Hz, 1 H), 6.75 (d, J = 15.7 Hz, 1 H), 6.77 (d, J = 15.7 Hz, 1 H); ^{13}C NMR δ 16.37, 16.53, 19.51, 20.63, 21.95, 23.45, 23.58, 26.21, 26.33, 27.55, 27.74, 31.29, 34.16, 40.76, 46.93, 65.52, 65.58, 74.32, 123.91, 124.07, 144.73, 144.81, 165.30; MS m/z 514 (<1) [M$^+$]. Anal. Calcd for C$_{32}$H$_{50}$O$_5$ (514.8): C, 74.67; H, 9.79. Found: C, 74.47; H, 9.66.

(1*R*,2*S*,5*R*)-8-Phenylmenthyl 3-(*E*)-[6-[2-(*E*)-(1*R*,2*S*,5*R*)-8-Phenylmenthoxycarbonylethenyl]-7-oxabicyclo[4.1.0]-hept-1-yl]acrylate (4e). Hexatriene **2e** (132 mg, 0.20 mmol) was reacted according to GP 4 with CF$_3$CO$_3$H (5.0 equiv, 1.0 mmol). CC on aluminum oxide (petroleum ether/EtOAc 20:1, column 3 × 14 cm) yielded 27 mg (21%) of the starting material **2e** (fraction I), 85 mg (63%) of the epoxide **4e** (fraction II, R_f = 0.18) as a colorless foam, and 11 mg of more highly oxidized products (fraction III): [α]$^{20}_D$ = −10.3 (c 1.00, CHCl$_3$); IR (cm^{-1}, KBr) 1712; ^{1}H NMR δ 0.82 (d, J = 6.3 Hz, 3 H), 0.84 (d, J = 6.3 Hz, 3 H), 0.91−1.71 (m, 16 H), 1.18 (s, 3 H), 1.21 (s, 3 H), 1.26 (s, 3 H), 1.28 (s, 3 H), 1.89 (m$_c$, 6 H), 2.02 (m$_c$, 2 H), 4.81 (m$_c$, 2 H), 5.36 (d, J = 15.8 Hz, 1 H), 5.38 (d, J = 15.8 Hz, 1 H), 6.28 (d, J = 15.8 Hz, 1 H), 6.42 (d, J = 15.8 Hz, 1 H), 7.13 (m$_c$, 4 H), 7.23−7.28 (m, 4 H); ^{13}C NMR δ 19.62, 21.75, 24.85, 25.22, 26.53, 27.50, 27.99, 31.24, 34.54, 39.65, 41.57, 50.37, 50.55, 65.26, 65.33, 74.50, 74.62, 123.84, 124.07, 124.85, 124.94, 125.35, 125.39, 127.97, 144.39, 144.54, 151.54, 151.68, 164.87, 164.94; MS m/z 666 (1) [M$^+$]. Anal. Calcd for C$_{44}$H$_{58}$O$_5$ (666.9): C, 79.24; H, 8.77. Found: C, 79.44; H, 8.79.

3,4-Diphenyl-11-oxabicyclo[4.4.1]undeca-1,5-diene (8a). A solution of 1,6-(*E*,*E*)-distyryl-7-oxabicyclo[4.1.0]heptane (**4a**) (50 mg, 0.17 mmol) in CCl$_4$/NEt$_3$ (1:1, 50 mL) was heated at 80 °C for 15 h. Careful monitoring of the reaction mixture showed no change in the composition within the last 3 h. After being cooled to rt and diluted with ether (200 mL), the reaction mixture was filtered and the filtrate concentrated in vacuo. The ^{1}H NMR spectrum of the crude residue showed a transformation of 60% of the starting material. CC on aluminum oxide (petroleum ether/Et$_2$O 10:1, column 10 × 1 cm) yielded 24 mg (48%) of **8a** as a colorless solid (fraction I, R_f = 0.59)

and 15 mg (30%) of the epoxide **4a** (fraction II, R_f = 0.42). After recrystallization from hexane, colorless crystals were obtained: mp 104 °C; ¹H NMR δ 1.79 (m$_c$, 2 H), 1.95 (m$_c$, 2 H), 2.29−2.57 (m, 4 H), 4.37 (m$_c$, 2 H), 4.97 (m$_c$, 2 H), 6.69 (m$_c$, 4 H), 7.06 (m$_c$, 6 H); ¹³C NMR δ 25.81, 33.47, 47.24, 114.42, 126.14, 127.50, 128.89, 141.47, 159.49; MS m/z 302 (52) [M⁺], calcd for $C_{22}H_{22}O$ 302.1670 (correct mass according to HRMS).

General Procedure for the Cope Rearrangement of the Dialkenylepoxides in Dioxane (GP 5). To a solution of the epoxide **4** (0.50 mmol) in anhydrous dioxane (15 mL) was added NEt₃ (140 μL, 1.00 mmol). The mixture was stirred for 1 d at the given temperature, cooled to rt, and concentrated in vacuo, and the residue was chromatographed on silica gel.

Dimethyl 11-Oxabicyclo[4.4.1]undeca-1,5-diene-3,4-dicarboxylate (8b). The diester epoxide **4b** (131 mg, 0.492 mmol) was reacted for 22 h at 60 °C according to GP 5. CC on silica gel [petroleum ether/EtOAc 15:1 (300 mL), then petroleum ether/EtOAc 10:1, column 3 × 17 cm] afforded 121 mg (92%) of **8b** (R_f = 0.33, petroleum ether/EtOAc 10:1) as a colorless solid: mp 57 °C; IR (cm⁻¹; KBr) 1738; ¹H NMR δ 1.52−1.66 (m, 2 H), 1.76−1.91 (m, 2 H), 2.18−2.41 (m, 4 H), 3.68 (s, 6 H), 4.16 (m$_c$, 2 H), 5.13 (m$_c$, 2 H); ¹³C NMR δ 25.47, 32.98, 42.80, 52.02, 109.28, 162.44, 172.81; MS m/z 266 (28) [M⁺]. Anal. Calcd for $C_{14}H_{18}O_5$ (266.3): C, 63.15; H, 6.81. Found: C, 63.27; H, 6.87.

Di-*tert*-butyl 11-Oxabicyclo[4.4.1]undeca-1,5-diene-3,4-dicarboxylate (8c). The diester epoxide **4c** (124 mg, 0.35 mmol) was reacted according to GP 5 at 80 °C for 19 h. CC on silica gel (petroleum ether/EtOAc 100: 3, column 2.5 × 17 cm) afforded 103 mg (83%) of the oxepine **8c** (R_f = 0.26) as a colorless solid: mp 97 °C; IR (cm⁻¹, KBr) 1730; ¹H NMR δ 1.41 (s, 18 H), 1.47−1.66 (m, 2 H), 1.74−1.92 (m, 2 H), 2.15−2.40 (m, 4 H), 3.96 (m$_c$, 2 H), 5.06 (m$_c$, 2 H); ¹³C NMR δ 25.56, 27.92, 33.04, 43.88, 80.71, 110.26, 161.84, 171.55; MS m/z 350 (<1) [M⁺]. Anal. Calcd for $C_{20}H_{30}O_5$ (350.5): C, 68.55; H, 8.63. Found: C, 68.53; H, 8.57.

Di-(1*R*,2*S*,5*R*)-menthyl 11-Oxabicyclo[4.4.1]undeca-1,5-diene-3,4-dicarboxylate (8d). The diester epoxide **4d** (60 mg, 0.12 mmol) was reacted for 17 h at 80 °C according to GP 5. CC on silica gel (petroleum ether/EtOAc 35:1, column 1.5 × 15 cm) afforded 53 mg (88%) of **8d** (R_f = 0.37) as a colorless foam: [α]²⁰$_D$ = −117.4 (*c* 0.89, CHCl₃); IR (cm⁻¹; film) 1731; ¹H NMR δ 0.70 (d, *J* = 6.4 Hz, 3 H), 0.72 (d, *J* = 6.4 Hz, 3 H), 0.80−1.09 (m, 18 H), 1.30−1.70 (m, 10 H), 1.75−1.98 (m, 6 H), 2.11−2.36 (m, 4 H), 3.96 (m$_c$, 1 H), 4.23 (m$_c$, 1 H), 4.64 (dt, *J* = 4.4, *J* = 10.9 Hz, 1 H), 4.67 (dt, *J* = 4.4, *J* = 10.9 Hz, 1 H), 4.97 (m$_c$, 1 H), 5.25 (d, *J* = 5.1 Hz, 1H); ¹³C NMR δ 16.02, 16.16, 20.82, 20.84, 21.97, 23.07, 23.20, 25.41, 25.45, 25.76, 26.12, 31.33, 31.34, 33.05, 33.13, 34.13, 34.17, 40.60, 42.00, 43.98, 46.93, 46.99, 74.69, 74.78, 109.94, 110.39, 161.07, 162.57, 171.74, 171.79; DCI MS (NH₃) m/z 516 (2) [M⁺ + H], 533 (100) [M⁺ + NH₄], 550 (51) [M⁺ + NH₃ + NH₄].

Di-(1*R*,2*S*,5*R*)-8-phenylmenthyl 11-Oxabicyclo[4.4.1]-undeca-1,5-diene-3,4-dicarboxylate (8e). The diester epoxide **4e** (30 mg, 0.045 mmol) was reacted for 17 h at 80 °C according to GP 5. CC on silica gel (petroleum ether/EtOAc 20:1, column 1.5 × 10 cm) afforded 25 mg (83%) of **8e** (R_f = 0.37) as a colorless foam: [α]²⁰$_D$ = −79.8 (*c* 1.20, CHCl₃); IR (cm⁻¹; film) 1733; ¹H NMR δ 0.76−2.26 (m, 23 H), 0.81 (d, *J* = 6.4 Hz, 3 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 1.17 (s, 3 H), 1.25 (s, 3 H), 1.29 (s, 3 H), 1.34 (s, 3 H), 2.40−2.57 (m, 1 H), 2.63 (m$_c$, 1 H), 3.74 (m$_c$, 1 H), 4.50 (m$_c$, 1 H), 4.74 (dt, *J* = 4.2, *J* = 10.6 Hz, 1 H), 4.83 (dt, *J* = 4.3, *J* = 10.9 Hz, 1 H), 5.27 (d, *J* = 5.9 Hz, 1 H), 7.12−7.37 (m, 10 H); ¹³C NMR δ 21.71, 21.82, 23.91, 24.24, 25.42, 25.64, 26.43, 26.92, 28.73, 29.53, 31.17, 31.22, 32.81, 33.19, 34.40, 34.73, 39.45, 40.27, 40.91, 41.03, 41.41, 44.69, 50.39, 74.76, 75.04, 108.78, 110.26, 125.12, 125.24, 125.34, 125.43, 127.96, 128.01, 151.09, 152.05, 159.55, 163.83, 170.61, 171.72; DCI MS (NH₃) m/z 668 (19) [M⁺ + H], 685 (100) [M⁺ + NH₄].

Rearrangement of 1,6-(*E*,*E*)-Distyryl-7-oxabicyclo-[4.1.0]heptane (4a) in Toluene-*d*₈ [Formation of 2,2-(*E*,*E*)-Distyrylcyclohexanone (10a)]. A solution of **4a** (20 mg, 66 μmol) in toluene-*d*₈ (1 mL) was heated at 110 °C for 5 h. The progress of the reaction was monitored by ¹H NMR

spectroscopy. In the first 60 min, signals of the oxepine system **8a** were detected, but they disappeared again upon further heating and only signals of a new main product increased steadily. Concentration of the reaction mixture in vacuo and CC on silica gel (petroleum ether/EtOAc 10:1, column 1 × 10 cm) yielded 13 mg (65%) of **10a** as a colorless oil (R_f = 0.55): IR (cm⁻¹, KBr) 1700; ¹H NMR δ 1.90 (m$_c$, 4 H), 2.17 (m$_c$, 2 H), 2.58 (m$_c$, 2 H), 6.34 (d, *J* = 16.5 Hz, 2 H), 6.46 (d, *J* = 16.5 Hz, 2 H), 7.19−7.42 (m, 10 H); ¹³C NMR δ 21.84, 27.34, 37.94, 39.67, 57.54, 126.34, 127.58, 128.54, 130.80, 132.40, 136.99, 211.23; MS m/z 302 (9) [M⁺]. Anal. Calcd for $C_{22}H_{22}O$: 302.1670 (correct mass according to HRMS).

2,2-(*E*,*E*)-Distyrylcyclohexanone (10a). To a solution of **4a** (32 mg, 0.11 mmol) in anhydrous ether (2 mL) was added BF₃·OEt₂ (10 μL, 80 μmol), and the mixture was stirred for 5 min. The mixture was diluted with ether (20 mL), washed with water, dried over MgSO₄, and concentrated in vacuo. CC on silica gel (petroleum ether/EtOAc 10:1, column 1 × 8 cm) yielded 29 mg (91%) of **10a**.

Rearrangement of 1,5-(*E*,*E*)-Distyryl-6-oxabicyclo-[3.1.0]hexane (3a) in Toluene-*d*₈ [Formation of 2,2-(*E*,*E*)-Distyrylcyclopentanone (9a)]. A solution of **3a** (20 mg, 69 μmol) in toluene-*d*₈ (1 mL) was heated in an NMR tube at 110 °C for 8 h. The progress of the reaction was monitored by ¹H NMR spectroscopy, which showed a continuous formation of one main product. Concentration of the reaction mixture in vacuo and CC on silica gel (petroleum ether/Et₂O 10:1, column 1 × 10 cm) yielded 15 mg (75%) of **9a** as a colorless solid (R_f = 0.10): mp = 96 °C; IR (cm⁻¹, KBr) 1734; ¹H NMR δ 2.03 (quin, *J* = 6.5 Hz, 2 H), 2.32 (t, *J* = 6.5 Hz, 2 H), 2.39 (t, *J* = 6.5 Hz, 2 H), 6.24 (d, *J* = 16.3 Hz, 2 H), 6.47 (d, *J* = 16.3 Hz, 2 H), 7.18−7.40 (m, 10 H); ¹³C NMR δ 19.01, 35.30, 37.29, 58.36, 126.38, 127.64, 128.54, 130.14, 130.88, 136.77, 217.10; MS m/z 288 (9) [M⁺]. Anal. Calcd for $C_{21}H_{20}O$: 288.1514 (correct mass according to HRMS).

Rearrangement of 1,5-(*E*,*E*)-Distyryl-6-oxabicyclo-[3.1.0]hexane (3a) under High Pressure (12 kbar) [Formation of 2,2-(*E*,*E*)-Distyrylcyclopentanone (9a)]. A solution of **3a** (50 mg, 0.17 mmol) in CH₂Cl₂ (5 mL) was subjected to a pressure of 12 kbar in a sealed Teflon tube for 14 h. Concentration of the reaction mixture in vacuo yielded 50 mg (quantitative) of **9a** as a colorless solid.

Methyl 3-(*E*)-[1-[2-(*E*)-Methoxycarbonylethenyl]-2-oxo-cyclopent-1-yl]acrylate (9b). A solution of the epoxide **3b** (63 mg, 0.25 mmol) in BF₃·OEt₂ (2 mL) was stirred for 30 min at room temperature. The mixture was diluted with ether (100 mL) and washed with NaHCO₃ (2 × 50 mL), dried over Na₂SO₄, and concentrated in vacuo. CC on silica gel (petroleum ether/ EtOAc 4:1, column size 1.5 × 10 cm) yielded 45 mg (71%) of **9b** (R_f = 0.34) as a colorless oil: IR (cm⁻¹, film) 1726; ¹H NMR δ 1.97 (m$_c$, 2 H), 2.22 (t, *J* = 6.8 Hz, 2 H), 2.34 (t, *J* = 7.5 Hz, 2 H), 3.72 (s, 6 H), 5.86 (d, *J* = 16.0 Hz, 2 H), 6.83 (d, *J* = 16.0 Hz, 2 H); ¹³C NMR δ 18.95, 34.26, 37.11, 51.79, 58.09, 122.89, 145.57, 166.02, 213.53; MS m/z 252 (49) [M⁺]. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.84; H, 6.59.

3-(*E*)-4-[1-[2-(*E*)-Methoxycarbonylethenyl]cyclopent-1-yl]-4-oxobutenoic Acid Methyl Ester (11b) and Methyl 3-(*E*)-[1-[2-(*E*)-Methoxycarbonylethenyl]-2-oxocyclohex-1-yl]acrylate (10b). A solution of the epoxide **4b** (78 mg, 0.29 mmol) in BF₃·OEt₂ (2 mL) was stirred for 10 min at room temperature. The mixture was diluted with ether (100 mL), washed with NaHCO₃ (2 × 50 mL), dried over Na₂SO₄, and concentrated in vacuo. CC on silica gel (petroleum ether/ EtOAc 7:1 (200 mL), then 4:1, column size 1.5 × 12 cm) yielded 52 mg (67%) of **11b** (R_f = 0.45, petroleum ether/EtOAc 5:1) as a colorless solid, mp 29 °C, and 10 mg (13%) of **10b** (R_f = 0.24, petroleum ether/EtOAc 5:1) as a colorless oil. **10b**: IR (cm⁻¹, film) 1725; ¹H NMR δ 1.86 (m$_c$, 4 H), 2.06 (m$_c$, 2 H), 2.34 (m$_c$, 2 H), 3.74 (s, 6 H), 5.77 (d, *J* = 16.2 Hz, 2 H), 7.06 (d, *J* = 16.2 Hz, 2 H); ¹³C NMR δ 21.41, 26.91, 36.82, 39.59, 51.83, 57.28, 122.98, 147.65, 166.10, 207.83; DCI MS (NH₃) m/z 284 (100) [M⁺ + NH₄]. **11b**: IR (cm⁻¹, film) 1730, 1699; ¹H NMR δ 1.59−1.80 (m, 6 H), 2.16−2.24 (m, 2 H), 3.72 (s, 3 H), 3.78 (s, 3 H), 5.79 (d, *J* = 16.0 Hz, 1 H), 6.78 (d, *J* = 15.4 Hz, 1 H),

7.01 (d, $J = 16.0$ Hz, 1 H), 7.23 (d, $J = 15.4$ Hz, 1 H); ^{13}C NMR δ 24.52, 34.00, 51.76, 52.32, 61.84, 121.71, 131.61, 136.50, 149.47, 165.71, 166.40, 197.29; DCI MS (NH$_3$) m/z 284 (100) [M$^+$ + NH$_4$]. Anal. Calcd for C$_{14}$H$_{18}$O$_5$ (266.3): C, 63.15; H, 6.81. Found: C, 62.88; H, 6.75.

Rearrangement of Methyl 3-(*E*)-[5-[2-(*E*)-Methoxycarbonylethenyl]-6-oxabicyclo[3.1.0]hex-1-yl]acrylate (3b) [Formation of Dimethyl Indan-5,6-dicarboxylate (12b)]. A solution of the epoxide **3b** (88 mg, 0.35 mmol) and NEt$_3$ (100 μL, 0.72 mmol) in a 1:1 mixture of anhydrous MeCN and THF (8 mL) was subjected to a pressure of 10 kbar at 70 °C for 3 d in a sealed Teflon tube. The reaction mixture was concentrated in vacuo and chromatographed on silica gel (petroleum ether/EtOAc 10:1, column 2.5 × 8 cm) to give 67 mg (82%) of **12b** (R_f = 0.29) as a colorless solid.[21]

Rearrangement of *tert*-Butyl 3-(*E*)-[5-[2-(*E*)-*tert*-Butoxycarbonylethenyl]-6-oxabicyclo[3.1.0]hex-1-yl]acrylate (3c) [Formation of Di-*tert*-butyl Indan-5,6-dicarboxylate (12c)]. A solution of the epoxide **3c** (62 mg, 0.18 mmol) and NEt$_3$ (51 μL, 0.37 mmol) in a 1:1 mixture of anhydrous MeCN and THF (8 mL) was subjected to a pressure of 10 kbar at 70 °C for 3 d in a sealed Teflon tube. The reaction mixture was concentrated in vacuo and chromatographed on aluminum oxide (petroleum ether/EtOAc 40:1, column 2.5 × 15 cm) to give 27 mg (46%) of **12c** (fraction I, R_f = 0.24) as a colorless solid, mp 59 °C, and 21 mg (34%) of starting material **3c** (fraction II): IR (cm^{-1}, KBr) 1718; ^{1}H NMR δ 1.57 (s, 18 H), 2.09 (quin, $J = 7.5$ Hz, 2 H), 2.92 (t, $J = 7.5$ Hz, 4 H), 7.46 (s, 2 H); ^{13}C NMR δ 25.37, 28.07, 32.66, 81.36, 124.59, 132.22, 146.88, 167.26; MS m/z 318 (3) [M$^+$]. Anal. Calcd for C$_{19}$H$_{26}$O$_4$: 318.1831 (correct mass according to HRMS).

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(21) Analytical data for **12b** and **13b**: Hillard, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058–4069.

Rearrangement of Methyl 3-(*E*)-[6-[2-(*E*)-Methoxycarbonylethenyl]-7-oxabicyclo[4.1.0]hex-1-yl]acrylate (4b) [Formation of Dimethyl 5,6,7,8-Tetrahydronaphthalene-2,3-dicarboxylate (13b)]. A solution of the epoxide **4b** (52 mg, 0.20 mmol) and NEt$_3$ (54 μL, 0.39 mmol) in anhydrous THF (8 mL) was subjected to a pressure of 10 kbar at 70 °C for 2 d in a sealed Teflon tube. The reaction mixture was concentrated in vacuo and chromatographed on silica gel (petroleum ether/EtOAc 7:1, column 2.5 × 12 cm) to give 35 mg (72%) of **13b** (R_f = 0.31) as a colorless solid.[21]

Supporting Information Available: ORTEP drawings, X-ray data, and details for the X-ray data acquisition for **8a**, ^{1}H NMR and ^{13}C NMR spectra of compounds **3b**, **8d**,**e**, **9a**, **10a**, and **12c**, low-resolution EIMS data and ^{13}C NMR DEPT data for all new compounds, and experimental procedures for epoxidations (Table 1, entries 4, 6, 7, 8, 9, and 11) and rearrangements (Table 2, entries 4, 6, and 19). This material is available free of charge via the Internet at http://pubs.acs.org.

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