83. Effects of Remote Substitution on the Photo-oxidation of Exocyclic s-cis-Butadienes Grafted onto Bicyclo [2.2.1]heptanes. Thermal and Rhodium Catalyzed Rearrangements of 3,6-Dihydro-1,2-dioxines[1])[2])

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Summary

The rates of photo-oxidation of exocyclic s-cis-butadienes grafted onto bicyclo-[2.2.1]heptanes and 7-oxabicyclo[2.2.1]heptanes (1-6) are dependent upon remote modifications of the bicyclic skeletons. They correlate with the rates of Diels-Alder additions of these dienes to strong dienophiles. The 2,3-dimethylidenenorbornane (1), 5,6-dimethylidene-2-norbornene (2) and 2,3-dimethylidene-7-oxanorbornane (3) gave the corresponding endo-peroxides (3,6-dihydro-1,2-dioxines) 7-9 in good yield. The 2,3,5,6-tetramethylidene-7-oxanorbornane (4) gave the mono-endo-peroxide 6, the latter did not react with a second equivalent of oxygen. Similarly, 5,6-dimethylidene-7-oxa-2-norbornene (5) was unreactive toward photo-oxidation. Thermal isomerization of the endo-peroxides 7 and 9 gave the trans-diepoxides 10 and 14, respectively, with high stereoselectivity. The endo-peroxides 6, 7 and 9 were cleanly isomerized into the corresponding α,β-unsaturated γ-hydroxy aldehydes in the presence of catalytic amounts of $Rh_2(CO)_4Cl_2$.

Introduction. – *Gorman et al.* [2] have studied the temperature dependence of the rate constants of the additions of singlet oxygen ($^1O_2$) to a large variety of furans and indoles in toluene. The enthalpies of activation ($\Delta H^{\neq}$) were found to be zero, whereas entropies of activation ($\Delta S^{\neq}$) fell in the range -18 to -34 cal mol^{-1} K^{-1}. The zero $\Delta H^{\neq}$-value was attributed to the electronically excited nature of $^1O_2$. The increase of the $\Delta S^{\neq}$-value with substitution in the dienes was interpreted in terms of steric acceleration due to a lowering of substituent entropy restrictions as the transition state of the rate-determining step was approached. An important consequence of the zero $\Delta H^{\neq}$-value is that the relative electron-donating abilities of the

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[1]) Interaction between non-conjugated chromophores, Part. 17. Part 16, see [1]. An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton.

[2]) This work has been presented at the 8th IUPAC Symposium on Photochemistry, in Seefeld, Austria, July 13-19, 1980.

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various substrates should not have a direct effect on the reactivity of the dienes toward $^1O_2$. Recently, *Monroe* [3] came up with the same conclusion for the 1,4-cycloadditions of $^1O_2$ to acyclic and cyclic dienes. This urges us to report our preliminary results on the sensitized photo-oxidation of 2,3-dimethylidene-bicyclo[2.2.1]heptane (**1**), 5,6-dimethylidene-2-bicyclo[2.2.1]heptene (**2**), the 7-oxabicyclo[2.2.1]heptane analogs **3** and **5**, of the 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**4**) and of its mono-*endo*-peroxide ($=3,6$-dihydro-1,2-dioxine) **6**. Since the distance separating the exocyclic methylidene C-atoms is expected not to vary significantly [4] between these dienes blocked in the *s-cis* conformation and pertubed only by remote modifications of the bicyclic skeleton, we expected only small reactivity differences between the photo-oxidation of these olefins. Strikingly and contrary to the conclusions of *Gorman et al.* [2] and *Monroe* [3], we have observed a very large reactivity difference between **1-6** toward singlet oxygen generated in solution by photosensitization.
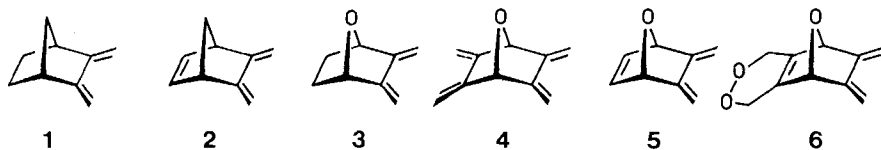

Results and discussion. – Sensitized photo-oxidation (5,10,15,20-tetraphenyl-porphine (TPP), CH_2Cl_2, iodine lamp, -50 to $+25°$) of the olefins **1-4** gave the corresponding *endo*-peroxides **6-9**. No other product could be detected. The triene **5** did not react under long exposure to the above conditions, only slow polymerization was observed. Variation of solvent (acetone, methanol, pentane, CCl_4 [5]) and sensitizer (methylene blue, Rose Bengale, polymer-immobilized Rose Bengale [6][5]) had no influence. The olefin **5** did not act as an inhibitor of the photo-oxidation of **1–4**, thus excluding the reversible formation of an unstable oxygen-diene adduct or charge-transfer complex. Similarly, the mono-*endo*-peroxide **6** was completely inert to sensitized photo-oxidation and did not add a second equivalent of O_2. DABCO (1,4-diazabicyclo[2.2.2]octane) [7] in concentration $<7\cdot10^{-3}$M [8] was found to inhibit the photo-oxidations of **1-4** (5-8 · 10^{-3}M, CH_2Cl_2, $-20°$), thus confirming the involvement of $^1O_2$ in the formation of the corresponding *endo*-peroxides **6-9**. For instance, when one mol-equiv. of DABCO was added to a $5\cdot10^{-3}$M solution of **1**, its rate of photo-oxidation was decreased by about 100. The structure of **6-9** was given by their spectral data and their rearranged products [9]. The *endo*-peroxides **7** and **9** were relatively stable and could be purified by distillation *in vacuo*. The adducts **6** and **8** were less stable and gave
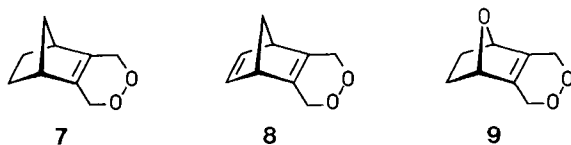
polymers upon heating. The diene **8** could be purified by silica gel column chromatography; **6** was decomposed under these conditions or in the presence of *Florisil!*

Thermal isomerization of **7** (degassed pentane, cyclohexane or benzene, 130°, 6 h) yielded the *trans*-diepoxide **10** as major product (57–70%), isolated [9] together with some α,β-unsaturated γ-hydroxy aldehyde **11** (5–15%), the furan **12** (1–5%) [10] and the dialdehyde **13** (5–15%). The same products were formed in the photolysis of **7** (quartz, 2537 Å Hg-lamp, pentane or acetone, −10°). Upon heating, the oxa-analog **9** (degassed C_6D_6, 130°, 4 h) gave the *trans*-diepoxide **14** (50%), the 7-oxabicyclo[2.2.1]heptane-2*exo*,3*endo*-dicarbaldehyde **17** (30%) together with polymers (<20%), but no **15** and **16**. The polyenes **1–4** were not generated (no cycloreversion giving O_2 [11]) upon heating their corresponding *endo*-peroxides. No trace of the *cis*-diepoxides **18–21** could be detected by GC, TLC and ^{1}H-NMR. The high stereoselectivity of the *endo*-peroxide → *trans*-diepoxide rearrangements can be rationalized by invoking stereoelectronic control and/or electronic repulsion between the O-atoms during the homolysis of the O,O-bond (see **22, 23**) and closure to **10** and **14**, respectively.

Z = CH₂: **10**   **11**   **12**   **13**
Z = O: **14**   **15**   **16**   **17**
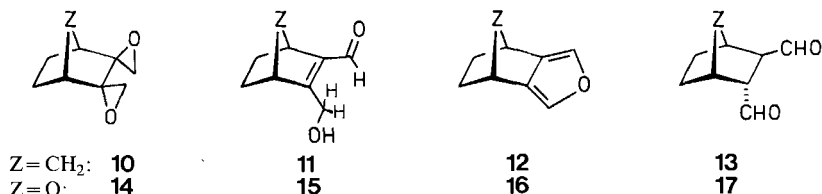
The diepoxide **10** was stable under the conditions of its formation. The analog **14** was less stable and was isomerized slowly into the dialdehyde **17** (benzene or gas phase, 130°). In acetonitrile saturated with brucine, **9** (0.6M, 20° 2 h) gave **17** as major product, probably *via* the α,β-unsaturated γ-hydroxy aldehyde **15**. Under the same conditions, **10** gave first **11** which was then slowly rearranged (several days, 25°) to **13**. The latter was obtained in good yield (92%) by stirring **7** in benzene with basic alumina (25°, 2 h).

In the presence of a catalytical amount of $Rh_2(CO)_4Cl_2$ [9], the *endo*-peroxides **7** and **9** were isomerized readily and in good yield to the α,β-unsaturated γ-hydroxy aldehydes **11** and **15**, respectively[6]). The same catalyzed rearrangement was

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[6]) Rhodium(I) complexes have been found to catalyze the cleavage of tetramethyl-1,2-dioxetane to acetone, probably by oxidative addition to the relatively weak O,O-bond [12]. A similar mechanism may also intervene in our *endo*-peroxide → α,β-unsaturated γ-hydroxy aldehyde rearrangements. This would imply the generation of 7-membered metallocyclic intermediates that would undergo facile β-hydrogen eliminations. We found that CuCl and $Fe(CO)_5$ did also catalyze the above rearrangements, but less efficiently than $Rh_2(CO)_4Cl_2$ (s. also [13]). The isomerizations were not due to acidic impurities (that could have been generated with alcoholic contaminants [14]) as it was found that added K_2CO_3 did not stop the reactions. By heating **11** in AcOH, the furan **12** was formed as major product. An analogous water elimination **15** → **16** + H_2O could not be achieved under acidic and basic conditions.

$$Z = CH_2: \quad \mathbf{18} \qquad\qquad \mathbf{19} \qquad\qquad \mathbf{22}$$
$$Z = O: \quad\;\; \mathbf{20} \qquad\qquad \mathbf{21} \qquad\qquad \mathbf{23}$$
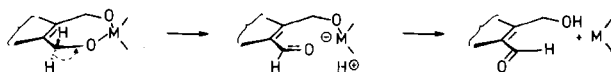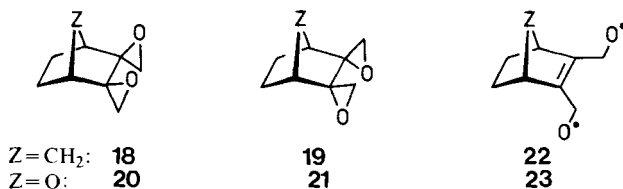
observed with **6**, leading to the unstable derivative **24** whose diastereomeric esters **25** obtained with $(-)$-a-methoxy-a-phenyl-a-(trifluoromethyl)acetyl chloride and pyridine [15] could be purified and characterized. The *Kornblum-DeLaMare* rearrangements [16] **7 → 11** and **9 → 15** could be achieved enantioselectively in the presence of catalytical amounts of optically active, natural bases [17].

24 R = H
25 R = $(CH_3O)(CF_3)(C_6H_5)CCO$
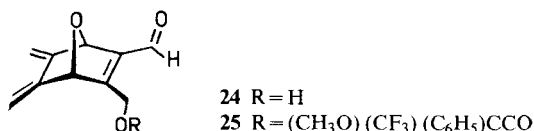
The relative rate of senzitized photo-oxidation of the olefins **1-6** were evaluated and are reported in the *Table*. The disparition of the olefins was measured by GC. and by ^{1}H-NMR. analyses of aliquots and were found to obey first-order rate laws $\ln[\text{olefin}] - \ln[\text{olefin}]_0 = -k(t - t_0)$. The comparative rates were determined for all the possible pairs of olefins **1-6**. None of these compounds did inhibit the photo-oxidation of the others.

We observed relatively large reactivity differences between **1-6** in their photo-oxidation. The rates of the formation of the *endo*-peroxides were parallel to those of the *Diels-Adler* additions to ethylenetetracarbonitrile (tetracyanoethylene; TCE). The variation of the rate constants of the latter reactions were shown to depend

Table. *Relative rate constants of the photo-oxidations of* **1-6** *and cyclopentadiene* (C_5H_6) (in CH_2Cl_2 at $-20°$), *rate constants of their cycloaddition to TCE* (in toluene, 25°) *and gas phase ionization potentials of* **1-5** *and* C_5H_6

Diene	**1**	**2**	**3**	**4**	**5**	**6**	C_5H_6
$k_{\mathrm{rel}}(^1O_2)^{\mathrm{a})}$	(1.0)	0.12 ± 0.015	0.07 ± 0.02	0.02 ± 0.01	$<0.001^{\mathrm{b})}$	$<0.001^{\mathrm{b})}$	>10
$k^{\mathrm{II}}(+\mathrm{TCE}, 25°)$ 690		53	5	1.5	<0.5	$0.004^{\mathrm{c})}$	$3.6 \cdot 10^{7\,\mathrm{d})}$
$[10^4\ \mathrm{mol}^{-1}\mathrm{s}^{-1}]$							
IP [eV]		8.41 8.48	8.79	8.60	8.87	–	8.58 [23]

a) For mixtures of two olefins (2 mmol) and 30 mg TPP in 300 ml CH_2Cl_2, $-20°$ bubbling and stirring with pure O_2, iodine lamp (*Phillips*, 24V/10A).
b) Less than 5% of the dienes **5** and **6** was polymerized after 8 h of irradiation; no trace of the corresponding *endo*-peroxides could be detected. Under these conditions, the half-life of **1** was 1.4–1.6 min.
c) Rate constant for the cycloaddition of the TCE monoadduct of the tetraene **4** [20].
d) Values obtained in CH_2Cl_2 at 20° [24]; see also values obtained in dioxane at 20°: 430 $\mathrm{mol}^{-1}\mathrm{s}^{-1}$ [25] and $951 \pm 46\ \mathrm{mol}^{-1}\mathrm{s}^{-1}$ [26].

mainly upon the $\Delta H^{\neq}$-term. Since the 1,4-distances separating the methylidene C-atoms of the exocyclic dienes blocked in the s-cis-conformation [18] does not vary significantly between **1**-**6** [4], the variation of the $\Delta H^{\neq}$-term was attributed to changes in the electron-donating ability of the dienes [19] (see IP's, *Table*) and in the exothermicity of the cycloadditions [20]. The arguments invoked by *Gorman et al.* [2] to interpret the reactivity difference of the $^1O_2$ additions to various dienes as being due to the variation of the $\Delta S^{\neq}$-term cannot be applied in the case of the photo-oxidations of **1**-**6** as these dienes have all the same substitution pattern in the diene moiety. If $^1O_2$ does indeed intervene in the formation of the *endo*-peroxides **6**-**9** (as suggested by the DABCO quenching experiments, s. however [21] for other possible mechanisms), we must assume a non-zero $\Delta H^{\neq}$-term for its cycloaddition to **1**-**6** that is affected by the electron-donating ability of the dienes and the exothermicity of the reactions. We do not see why the reactivity difference observed between our exocyclic dienes should be due to differential solvent effects on the $\Delta S^{\neq}$-term. Correlation between rates of photo-oxidation and *Diels-Adler* additions of dienes have been reported several times [22].

Conclusion. – Contrary to predictions based on the recent work of *Gorman et al.* [2] and *Monroe* [3], the sensitized photo-oxidation of exocyclic dienes maintained in the s-cis conformation depend strongly upon remote modifications of the bearing bicyclic skeleton. If the mechanism of the formation of the *endo*-peroxides **6**-**9** is the same as that of the $^1O_2$-additions to other dienes [2] [3], our result are most simply interpreted by admitting non-zero $\Delta H^{\neq}$-values for the photo-oxidations of **1**-**6**. More work is definitely required if one wishes to understand the details of the 1,4-additions of singlet oxygen. The mechanism could well be substrate-dependent.

The thermal isomerizations of the *endo*-peroxides **7** and **9** are highly stereoselective and yield the *trans*-diepoxides **10** and **14**, respectively. $Rh_2(CO)_4Cl_2$ is a very good catalyst for the delicate rearrangements of 3,6-dihydro-1,2-dioxines into α,β-unsaturated γ-hydroxy aldehydes.

Experimental Part.

General remarks. See [27]. NMR. attributions were confirmed by double irradiation experiments. The olefins **1** [28], **2** [29], **3** [30], **4** [27] and **5** [31] were prepared according to known procedures. They were purified by distillation *i. v.* just before use.

Synthesis of 4,5-dioxatricyclo[6.2.1.0²,⁷]undec-2(7)-ene. (**7**). See [10].

Synthesis of 4,5-dioxatricyclo[6.2.1.0²,⁷]undeca-2(7),9-diene (**8**). The triene **2** (1 g, 8.2 mmol) in freshly distilled CH_2Cl_2 (400 ml) containing TPP (30 mg, 0.049 mmol, *Fluka*) was irradiated (iodine lamp, 24V/10A, *Phillips*, Pyrex vessel, 0°) while bubbling pure O_2 through the solution. After disparition of the diene (*ca.* 2 h, by TLC.), the solvent was evaporated and the residue (> 95% of **8** by ¹H-NMR.) purified by column chromatography on silica gel (ether/hexane) yielding 0.95 g (77%) of **8** as a colorless oil that polymerizes upon heating *i. v.* (10^{-3} Torr) at 25° without formation of **2**. - UV. (isooctane): final absorption. - IR. (CHCl₃): 2990, 2970, 2890, 2840, 1560, 1450, 1430, 1350, 1295, 1260, 1225, 1200, 1120, 1040, 1030, 975. - ¹H-NMR. (CD₂Cl₂): 6.77 ($d \times d$, $^3J = {}^4J = 1.8$, H–C(9) and H–C(10)); 4.84 and 4.33 ($2\,d \times m$, $^2J = 15$ each, each 2 H, H₂C(3) and H₂C(6)); 3.49 (*m*, H–C(1) and H–C(8)); 2.05 (*m*,

$H_2C(11)$). – ^{13}C-NMR. (CDCl$_3$): 144.8 (m, C(2) and C(7)); 142.2 (d×m, ^1J(C,H)= 174.9, C(9) and C(10); 71.7 (t×m, ^1J(C,H)= 143.7, H$_2$C(3) and H$_2$C(6)); 71.3 (t×m, ^1J(C,H)= 136.4, C(11)); 49.5 (qa×d, ^1J(C,H)= 149.2, $^n J$(C,H)= 8.2, C(1) and C(8)). – MS. (70 eV): 150 (63), 129 (73), 128 (98), 103 (18), 92 (28), 91 (100), 90 (25), 77 (33), 66 (52), 65 (35).

$$C_9H_{10}O_2 \ (150.17) \quad \text{Calc. C } 71.98 \quad \text{H } 6.71\% \quad \text{Found C } 71.93 \quad \text{H } 6.70\%$$

Synthesis of 4,5,11-trioxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (**9**). Same procedure as for the preparation of **8**, using the diene **3** (1 g, 4-5 h irradiation time). After evaporation of the solvent, the crude **9** (>95% pure by ^{1}H-NMR.) was distilled *i. v.* (70°/10^{-3} Torr, bulb-to-bulb distillation yielding 0.94 g (74%) of **9** as colorless crystals, m.p. 57–59°. – UV. (isooctane): final absorption. – IR. (CHCl$_3$): 3010, 2970, 2910, 2840, 1470, 1450, 1430, 1355, 1320, 1290, 1270, 1180, 1155, 1115, 1005, 955, 935, 920, 875, 825. – ^{1}H-NMR. (CDCl$_3$): 5.02 (m, H–C(1) and H–C(8)); 4.89 and 4.55 (2 d×m, ^2J= 15 each, 2 H each, H$_2$C(3) and H$_2$C(6)); 1.89 (d×m, Hexo-C(9) and Hexo-C(10)); 1.28 (d×d, ^2J= 10, ^3J= 2.6, Hendo–C(9) and Hendo–C(10)). – ^{13}C-NMR. (CDCl$_3$): 137.9 (m, C(2) and C(7)); 77.8 (d×d×m, ^1J(C,H)= 163.9, ^3J(C,H)= 8.2, C(1) and C(8)); 68.2 (t×m, ^1J(C,H)= 145.6, H$_2$C(3) and H$_2$C(6)); 24.8 (t×m, ^1J(C,H)= 136.4, C(9) and C(10)). – MS. (70 eV): 154 (35), 127 (70), 126 (96), 125 (36), 108 (80), 95 (70), 94 (95), 81 (29), 80 (30), 79 (39), 77 (100), 67 (33), 55 (23), 53 (16), 41 (43), 39 (37).

$$C_8H_{10}O_3 \ (154.17) \quad \text{Calc. C } 62.33 \quad \text{H } 6.54\% \quad \text{Found C } 62.23 \quad \text{H } 6.55\%$$

Synthesis of 9,10-dimethylidene-4,5,11-trioxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (**6**). Same procedure as for the preparation of **8**, using **4** (1 g, 6-7 h irradiation time) and CH$_2$Cl$_2$ freshly distilled from NaHCO$_3$. After evaporation of the solvent, the crude **6** (>95% by ^{1}H-NMR.) was used directly in the next reactions. – ^{1}H-NMR. (CDCl$_3$): 5.33 and 5.14 (2 s, 2 H each, H$_2$C=C(9) and H$_2$C=C(10)); 5.16 (br.s, H–C(1) and H–C(8)); 4.94 and 4.55 (2 d×m, ^2J= 15 each, 2 H each, H$_2$C(3) and H$_2$C(6)). – ^{13}C-NMR. (CDCl$_3$): 142.1 (m, C(9) and C(10)); 139.2 (m, C(2) and C(7)); 102.5 (t, ^1J(C,H)= 160.2, H$_2$C=C(9) and H$_2$C=C(10)); 82.4 (d×m, ^1J(C,H)= 170, ^3J(C,H)= 10, C(1) and C(8)); 68.3 (t, ^1J(C,H)= 146.5 C(3) and C(6)).

Synthesis of 2exo,2endo:3endo,3exo-bis(epoxymethano)bicyclo[2.2.1]heptane (**10**). The *endo*-peroxide **7** (0.4 g, 2.6 mmol) in degassed pentane (30 ml) was heated in a sealed Pyrex tube *i.v.* to 130° for 6 h. After cooling to r.t., the tube was opened and the solvent evaporated *i.v.* The residue contained **10** (68%), **11** (15%), **13** (15%) and **12** (1%), identified and analyzed by ^{1}H-NMR. and GC. Bulb-to-bulb distillation at 25-50°/10^{-2} Torr yielded a first fraction composed of **12** [10] (11 mg, 3%). Second fraction: 252 mg (63%) of pure **10** as a colorless liquid. – UV. (isooctane): final absorption. – IR. (CHCl$_3$): 2975, 2885, 1490, 1455, 1390, 1310, 1300, 1220, 1115, 1095, 1075, 1020, 960, 930, 880, 875, 850, 830, 810. – ^{1}H-NMR. (CD$_3$COCD$_3$): 2.94 (d, ^2J= 5.2, 1 H, one of H$_2$C–C(2)); 2.84 (d, ^2J= 4.6, 1 H, the other of H$_2$C–C(2)); 2.75 (d, ^2J= 5.2, 1 H, one of H$_2$C–C(3)); 2.63 (d, ^2J= 4.6, 1 H, the other of H$_2$C–C(3)); 2.4-1.3 (m, 8 H, H–C(1), H–C(4), H$_2$C(5), H$_2$C(6) and H$_2$C(7)). – ^{13}C-NMR. (CDCl$_3$): 67.7 and 67.00 (2 m, C(2) and C(3)); 49.5 and 46.5 (2 t×m, ^1J(C,H)= 175 each, 2 C, CH$_2$–C(2) and CH$_2$–C(3)); 43.5 and 41.8 (2 d×m, ^1J= 148 each, C(1) and C(4)); 36.2 (t×m, ^1J(C,H)= 135, C(7)); 26.3 and 23.8 (2 t×m, ^1J(C,H)= 135 each, C(5) and C(6)). – MS. (70 eV): 152 (2), 124 (10), 107 (13), 94 (67), 93 (80), 91 (33), 79 (100), 77 (43), 68 (33), 67 (43), 66 (60), 65 (40), 55 (40), 53 (50), 51 (33).

$$C_9H_{12}O_2 \ (152.18) \quad \text{Calc. C } 71.03 \quad \text{H } 7.95\% \quad \text{Found C } 70.99 \quad \text{H } 8.01\%$$

Synthesis of 2exo,2endo:3endo,3exo-bis(epoxymethano)-7-oxabicyclo[2.2.1]heptane (**14**). The *endo*-peroxide **9** (0.5 g, 3.25 mmol) in degassed C$_6$D$_6$ was heated in a sealed Pyrex tube to 130° for 4 h. The mixture contained **14** (50%), **17** (30%) and polymers (*ca.* 20%); they were separated by prep. GC. (*OV/227*, length: 315 cm, diameter: 0.7 cm, He, 130°). The first fraction contained **14** (0.15 g, 30%), colorless oil. – UV. (isooctane): final absorption. – IR. (CDCl$_3$): 3070, 2980, 2880, 1490, 1460, 1445, 1405, 1205, 1260, 1200, 1110. – ^{1}H-NMR. (CDCl$_3$): 4.16 (m, H–C(1) and H–C(4)); 2.99 (d, ^2J= 5.0, 1 H); 2.78 (d, ^2J= 4.5, 1 H); 2.74 (d, ^2J= 5.0, 1 H); 2.62 (d, ^2J= 4.5, 1 H); 2.1-1.7 (m, H$_2$C(5) and H$_2$C(6)). – ^{13}C-NMR. (CDCl$_3$): 80.8 (d×d, ^1J(C,H)= 162.0, ^3J(C,H)= 7.3, C(1) or C(4)); 77.1 (d×d, ^1J(C,H)= 161.6, ^3J(C,H)= 7.8, C(4) or C(1)); 65.5 and 65.4 (2 br.s, C(2) and C(3)); 49.5 (t×d,

^1J(C,H)= 177.2, ^3J(C,H)≑2.3[7]), H_2C_{exo}–C(3)); 45.2 ($d\times d$, ^1J(C,H)= 174.8 and 177.6, ^3J(C,H)≈0, H_2C_{endo}–C(2)); 26.4 ($t\times m$, ^1J(C,H)= 136.4, C(5) or C(6)); 24.5 ($t\times m$, ^1J(C,H)= 133.7, C(6) or C(5)). – MS. (70 eV): 154 (44), 122 (12), 98 (24), 97 (41), 96 (91), 95 (91), 83 (41), 81 (41), 79 (41), 69 (47), 68 (53), 67 (100), 66 (47), 65 (14), 53 (50), 55 (62), 43 (21), 41 (32), 39 (56).

$C_8H_{10}O_3$ (154.17)   Calc. C 62.33 H 6.54%   Found C 62.27 H 6.50%

Synthesis of 7-oxabicyclo [2.2.1]heptane-2exo,3endo-dicarbaldehyde (**17**). The second fraction of the above prep. GC. contained **17** (0.15 g, 30%, formed in part by rearrangement of **14** in the injector), colorless oil, polymerizes rapidly at r.t. in the condensed phase. – IR. (CHCl₃): 3040, 2840, 2740, 1730, 1600, 1525, 1425, 1220, 1140, 1045, 1025. – ¹H-NMR. (CDCl₃): 9.83 (*s, endo*-CHO); 9.69 (*s, exo*-CHO); 5.0 (*m*, H–C(1) and H–C(4)); 3.63 ($d\times d$, ^3J=4.8 and 5.0, *Hexo*–C(3)); 3.11 (*d*, ^3J=5.0, *Hendo*–C(2)); 2.0–1.5 (*m*, H_2C(5) and H_2C(6)). – MS. (70 eV): 125 (11), 110 (7), 97 (11), 81 (57), 79 (29), 77 (29), 70 (22), 69 (28), 68 (29), 67 (21), 55 (43), 53 (43), 51 (29), 43 (28), 41 (99), 39 (100), 29 (57).

$C_8H_{10}O_3$ (154.17)   Calc. C 62.33 H 6.54%   Found C 62.24 H 6.53%

Synthesis of bicyclo [2.2.1]heptane-2exo,3endo-dicarbaldehyde (**13**). The *endo*-peroxide **7** (0.6 g, 3.95 mmol) and basic alumina (1.8 g) were stirred in benzene (5 ml) under N₂ at 25° for 12 h. The reaction was followed by TLC. on silica gel (ether/hexane 1:10, Rf of 7 0.65; Rf of 13 0.15). The alumina was filtered off and washed with ether (2 times 1 ml). After evaporation of the solvent *i.v.*, the residue was purified by rapid chromatography on a column of silica gel (AcOEt/hexane 1:2) yielding 0.552 g (92%) of **13** as a viscous, colorless oil that polymerizes at r.t. in the condensed phase. – IR. (CHCl₃): 2965, 2880, 2820, 2725, 1725, 1450, 1380, 1300, 1270, 1120, 1075, 975, 900. – ¹H-NMR. (CDCl₃): 9.75 and 9.65 (*s*, 2 CHO); 3.35 ($d\times d$, ^3J=5.4 and 4.5, H–C(3)); 2.95 (*d*, ^3J=5.4, H–C(2)); 2.91 (*m*, H–C(4)); 2.72 (*m*, H–C(1)); 1.9–1.12 (*m*, H_2C(5), H_2C(6) and H_2C(7)). – ¹³C-NMR. (CDCl₃): 201.8 ($d\times t$, ^1J(C,H)= 172.1, ^3J(C,H)≑5, *endo*-CHO); 200.6 ($d\times t\times d$, ^1J(C,H)= 172.1, ^3J(C,H)=7.4 and 3.7, *exo*-CHO[7])); 53.3 ($d\times d\times m$, ^1J(C,H)= 131.8, ^2J=23, C(2) and C(3)); 38.6 and 37.7 ($d\times m$, ^1J(C,H) =145.6, C(1) and C(4)); 37.3 ($t\times m$, ^1J(C,H)= 134.6, ^3J(C,H)=5.6, C(7)); 28.8 and 24.5 (2 $t\times m$, ^1J(C,H)= 132, C(5) and C(6)). – MS. (70 eV): 154 (5), 153 (44), 151 (4), 136 (8), 135 (100), 125 (4), 123 (4), 107 (14), 85 (7), 83 (10), 75 (9), 57 (7).

$C_9H_{12}O_2$ (152.18)   Calc. C 71.03 H 7.95%   Found C 71.15 H 7.77%

Synthesis of 3-hydroxymethyl-2-bicyclo[2.2.1]heptene-2-carbaldehyde (**11**). The *endo*-peroxide **7** (0.6 g, 3.95 mmol), Rh₂(CO)₄Cl₂ (60 mg, 0.15 mmol) and freshly distilled CHCl₃ (40 ml) were stirred under N₂ at 25° for 12 h. The end of the isomerization was checked by TLC., Rf of **11** 0.5 (ether). After evaporation of the solvent *i.v.* the residue was purified by rapid column chromatography on silica gel (ether) giving **11** as a colorless oil (0.432 g, 72%). It polymerizes rapidly at r.t. in the condensed phase. – IR. (CHCl₃): 3630 narrow (free OH), ∼3450 (intermolecular bridging of OH), 2970, 2880, 1665, 1585, 1450, 1380, 1360, 1325, 1225, 1175, 1110, 1025. Upon dilution the absorption at 3450 was reduced more than that at 3630, thus confirming the *s-trans* configuration of the α,β-unsaturated γ-hydroxy aldehyde. This effect was more important in CCl₄ than in CH₂Cl₂ (absence of intramolecular CH₂OH/CHO-bridging). – ¹H-NMR. (CDCl₃): 10.11 (*s*, CHO); 4.70 (*s*, CH₂OH); 4.46 (br.*s*, HO); 3.39 (*m*, H–C(1)); 3.13 (*m*, H–C(4)); 2.09–1.0 (*m*, H_2C(5), H_2C(6) and H_2C(7)). – ¹³C-NMR. (CDCl₃): 188.3 (*d*, ^1J(C,H)= 175.4, CHO); 167.6 (br.*s*, C(3)); 142.7 (br.*s*×*d*, ^2J(C,HC=O)= 24 [33], C(2)); 58.7 (*t*, ^1J(C,H)= 142.5, CH₂OH); 45.8 ($t\times t$, ^1J(C,H)= 135, ^3J(C,H)= 12, C(7)); 45.5 ($d\times m$, ^1J(C,H)= 147.0, C(1)); 40.1 ($d\times m$, ^1J(C,H)= 150, C(4)); 25.4 and 24.7 ($t\times m$, ^1J(C,H)= 135, C(5) and C(6)).

$C_9H_{12}O_2$ (152.18)   Calc. C 71.03 H 7.95%   Found C 70.97 H 7.90%

Synthesis of 3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-2-ene-2-carbaldehyde (**15**). Same procedure as for the preparation of **11**, using **9**. Aldehyde **15** was polymerized rapidly upon concentration at r.t.

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[7]   Vicinal ^3J(C,H)-coupling constants between the bridgehead H-atoms and the C-atoms of the epoxymethano and formyl substituents allow recognition of the *exo*- *vs. endo*-configuration [32].

and could not be purified. ^{1}H-NMR. of the reaction mixture indicated a yield > 95% for the Rh(II)-catalyzed isomerization. – ^{1}H-NMR. (CDCl$_3$): 9.98 (s, CHO); 5.25 and 5.01 (2 $d \times m$, $^3J = 3.5$ each, H–C(1) and H–C(4)); 4.61 (s, CH$_2$OH); 3.51 (br.s, HO); 2.0–1.7 (m, Hexo–C(5) and Hexo–C(6)); 1.24 ($d \times d$, $^2J = 10.8$, $^3J = 4.1$, Hendo–C(5) and Hendo–C(6)). – ^{13}C-NMR. (CDCl$_3$): 179.8 (d, $^1J(C,H) = 179.4$, CHO); 164.1 (br.s, C(3)); 141.5 ($d \times m$, $^2J(C, HC=O) = 24.1$ [33], C(2)); 79.9 ($d \times m$, $^1J(C,H) = 165$, C(1)); 77.4 ($d \times m$, $^1J(C,H) = 166$, C(4)); 57.7 (t, $^1J(C,H) = 142.4$, CH$_2$OH); 24.8 and 23.8 (2 $d \times m$, $^1J(C,H) = 137$, C(5) and C(6)).

Synthesis of 3-[(α-methoxy-α-(trifluoromethyl)acetoxy)methyl]-7-oxabicyclo[2.2.1]hept-2-ene-2-carbaldehyde from **15**. (–)-α-Methoxy-α-phenyl-α-(trifluoromethyl)acetyl chloride (252 mg, 1 mmol [15]) was added to the CHCl$_3$ (2 ml) solution of **15** obtained by Rh$_2$(CO)$_4$Cl$_2$-catalyzed isomerization of **11** (154 mg, 1 mmol). Under stirring, pyridine (79 mg, 1 mmol) in CHCl$_3$ (1 ml) was added dropwise. Pyridinium chloride was filtered off and the solvent evaporated *i.v.* The residue was purified by column chromatography on silica gel (10 g, AcOEt/hexane 3:1) yielding 262 mg (72%) of **15** as a colorless oil. – UV. (isooctane): 243 (8150), 210.5 (9500). – IR. (CHCl$_3$): 3000, 2970, 2860, 1765, 1675, 1500, 1460, 1275, 1175, 1125, 1090, 1020, 1005, 970, 940, 910. – ^{1}H-NMR. (CDCl$_3$): 9.93 (s, CHO); 7.60 (br.s, C$_6$H$_5$); 5.55 and 5.39 (AB, $^2J = 15$), and 5.58 and 5.33 (AB, $^2J = 15$, total 2 H, H$_2$C–C(3) of the 2 diastereo-isomers); 5.28 and 5.04 (2 $d \times m$, $^3J = 3.0$ each, H–C(1) and H–C(4)); 3.6 (s, CH$_3$O); 2.07–1.05 (m, H$_2$C(5) and H$_2$C(6)). – ^{13}C-NMR. (CDCl$_3$): 184.9 (d, $^1J(C,H) = 175.8$, CHO); 166.0 (br.s, CCOO); 154.7 (br.s, C(3)); 144.0 ($d \times m$, $^2J(C, HC=O) = 26.6$, C(2)); 129.7, 128.3 and 126.6 (3 $d \times m$, $^1J(C,H) = 164$ each, C$_6$H$_5$); 113.3 (s, CCOO); 80.1 ($d \times m$, $^1J(C,H) = 166.6$, C(1)); 77.4 ($d \times m$, $^1J(C,H) = 170.3$, C(4)); 58.9 (t, $^1J(C,H) = 150.6$, CH$_2$–C(3)); 55.2 (qa, $^1J(C,H) = 144.6$, CH$_3$O); 24.2 and 23.6 (2 $t \times m$, $^1J(C,H) = 136.4$ each, C(5) and C(6)). – ^{19}F-NMR. (CDCl$_3$, δ(CFCl$_3$) = 0 ppm, *Bruker HX 90*): 59.05 and 59.13. – MS. (70 eV): 370 (0.1), 190 (10), 189 (100), 186 (2), 158 (2), 141 (6), 139 (8), 137 (10), 136 (7), 127 (10), 119 (22), 109 (47), 108 (14), 105 (29), 91 (11), 81 (10), 79 (10), 77 (20).

C$_{18}$H$_{17}$F$_3$O$_5$ (370.33)   Calc. C 58.38 H 4.63%   Found C 58.43 H 4.65%

Synthesis of 3-[(α-methoxy-α-phenyl-α-(trifluoromethyl)acetoxy)methyl]-2-bicyclo[2.2.1]heptene-2-carbaldehyde from **11**. Same procedure as above, using a CHCl$_3$ solution of **11** (152 mg, 1 mmol). Yield: 225 mg (61%), colorless oil. – UV. (isooctane): 253 (11700), 210 (8400). – IR. (CHCl$_3$): 2950, 2880, 1745, 1655, 1445, 1350, 1265, 1160, 1115, 1075, 1000. – ^{1}H-NMR. (CDCl$_3$): 9.85 (s, CHO); 7.46 (m, C$_6$H$_5$); 5.41 and 5.11 (AB, $^2J = 14.5$, H$_2$C–C(3) of one diastereomer); 5.33 and 5.19 (AB, $^2J = 14.5$, H$_2$C–C(3) of the diastereomer); 3.54 (br.s, CH$_3$O); 3.37 and 3.02 (2 m, H–C(1) and H–C(4)); 2.07–0.85 (m, H$_2$C(5), H$_2$C(6) and H$_2$C(7)). – ^{13}C-NMR. (CDCl$_3$): 186.1 (d, $^1J(C,H) = 174$, CHO); 166.1 (br.s, CCOO); 157.6 (br.s, C(3)); 145.5 (d, $^2J(C,H) = 20$, C(2)); 129.7, 128.4 and 127.1 (3 $d \times m$, $^1J(C,H) = 163$ each, C$_6$H$_5$); 113.6 (s, CCOO); 60.0 (t, $^1J(C,H) = 150$, CH$_2$–C(3)); 55.2 (qa, $^1J(C,H) = 146.5$, CH$_3$O); 46.1 ($t \times t$, $^1J(C,H) = 135$, $^3J(C,H) = 7.3$, C(7)); 45.9 ($d \times m$, $^1J(C,H) = 146.5$, C(1)); 40.5 ($d \times t$, $^1J(C,H) = 146.6$, $^3J(C,H) = 6.4$, C(4)); 25.1 and 24.7 (2 $t \times m$, $^1J(C,H) = 134$ each, C(5) and C(6)). – ^{19}F-NMR. (CDCl$_3$): 58.71 and 58.66. – MS. (70 eV): 369 (13), 289 (3), 235 (3), 202 (3), 199 (13), 151 (9), 136 (9), 135 (100), 123 (11).

C$_{19}$H$_{19}$O$_4$F$_4$ (368.33)   Calc. C 61.96 H 5.20%   Found C 61.82 H 5.33%

Synthesis of 3-hydroxymethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-2-carbaldehyde (**24**). The *endo*-peroxide **6** (0.1 g, 0.56 mmol) and Rh$_2$(CO)$_4$Cl$_2$ (22 mg, 0.06 mmol) in CDCl$_3$ (0.5 ml) were stirred at r.t. for 6 h. The ^{1}H-NMR. of this solution showed **24** as major compound (> 95%): 10.0 (s, 1 H); 5.1–5.5 (br.s and m, 6 H); 4.6 (s, CH$_2$O); 3.5–3.0 (br.s, HO). All attempts to isolate **24** failed because it polymerized upon concentration.

Synthesis of 3-[(α-methoxy-α-phenyl-α-(trifluoromethyl)acetoxy)methyl]-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-2-carbaldehyde (**25**). (–)-α-Methoxy-α-phenyl-α-(trifluoromethyl)acetyl chloride (0.15 g, 0.6 mmol) [15]) was added to the solution of **24** obtained above, followed by the addition of pyridine (50 mg, 0.63 mmol). After stirring at r.t. for 10 min, the solution was evaporated *i.v.* and the residue purified by TLC. on silica gel (ether). The ester mixture **25** was collected as a colorless oil (20 mg, 9%), that polymerized readily upon concentration or/and heating. – ^{1}H-NMR. (CDCl$_3$): 9.9 (s, CHO); 7.5 (br.s, C$_6$H$_5$); 5.5–5.0 (4s and m, H$_2$C=C(5), H$_2$C=C(6), H–C(1), H–C(4), H$_2$C–C(3)); 3.5 (s, CH$_3$O). – MS. (70 eV): 394 (1), 365 (2), 275 (3), 189 (73), 132 (27), 119 (28), 105 (61), 91 (41), 77 (100), 70 (38).

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