Synthesis and Chemistry of Endoperoxides Derived from 3,4-Dihydroazulen-1(2*H*)-one: An Entry to Cyclopentane-Anellated Tropone Derivatives

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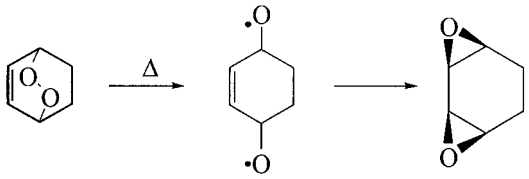
Reduction of trienone **1** and subsequent treatment with acid in MeOH furnished 1-methoxy-1,2,3,4-tetrahydroazulene (**13**). Photo-oxygenation of **13** provided the two bicyclic endoperoxides **14** and **15**. Pyrolysis of **14** and **15** gave the corresponding bis-epoxides **17** and **18**, which have been synthesized also upon treatment with a catalytic amount of CoTPP (TPP = tetraphenylporphyrin). That an unusual endoperoxide-endoperoxide rearrangement has not been observed strongly supports the assumption that the carbonyl group in **2**–**4** is responsible for this unprecedented endoperoxide-endoperoxide rearrangement. Treatment of the endoperoxides **14** and **15** with a catalytic amount of Et_3N at 0° provided the azulenones **22** and **23** in high yield. Attempted cleavage of the O–O peroxide linkage in **14** and **15** with thiourea resulted, contrary to our expectation, in the formation of **22** and **23**. That thiourea acts as a base instead of a reducing reagent has been observed for the first time in peroxide chemistry.

Introduction. – Bicyclic endoperoxides are known to undergo versatile chemical transformations [1]. One of the general reactions is the thermal cleavage of the weak O–O bond, followed by the addition of the oxygen radicals to the adjacent double bond to give *syn*-bis-epoxides (*Scheme 1*) [2].

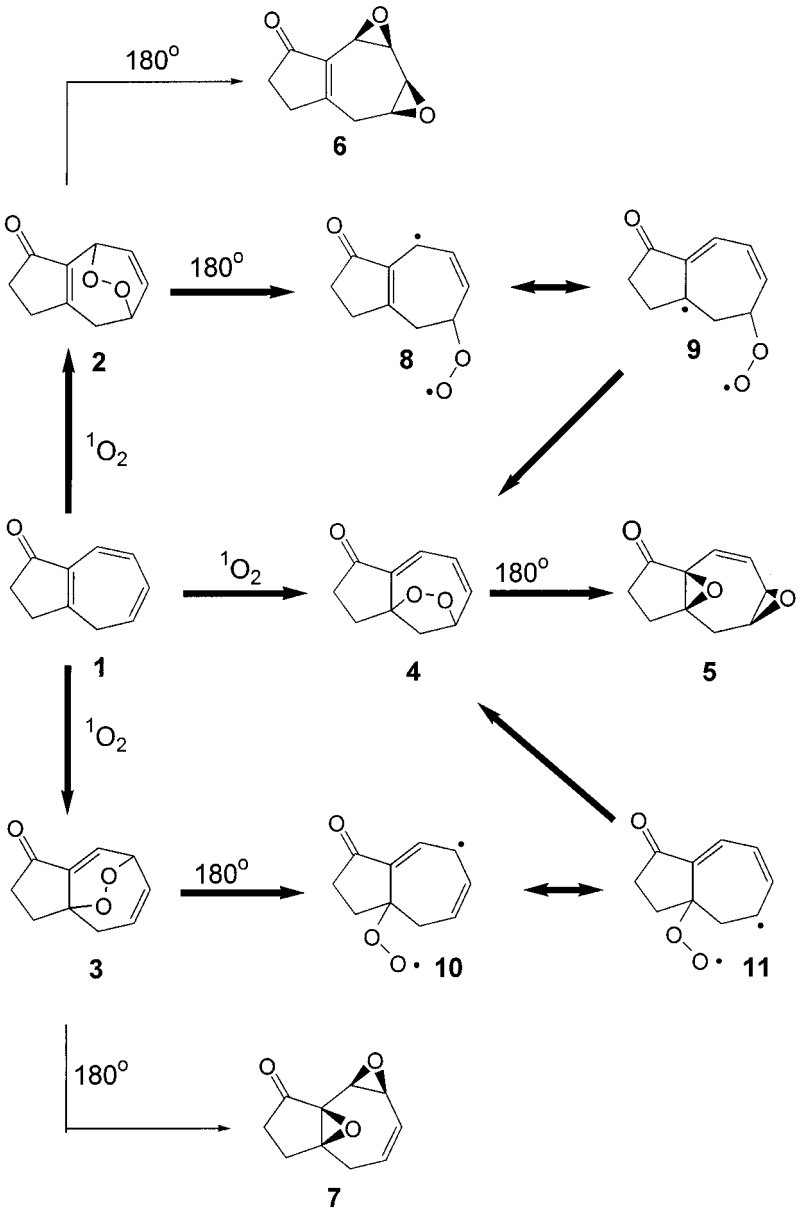
Scheme 1



In cases where significant resonance stabilization may result, the C–O bond of bicyclic endoperoxides can also be cleaved. Thus, heating of certain arene endoperoxides generates singlet oxygen and the corresponding aromatic compounds [3].

Scott and *Adams* [4] have studied the photo-oxygenation reaction of the bicyclic trienone **1** and its conversion to quinones of azulene. They reported that trienone **1** reacts with $^1O_2$ to produce **2** and **3** (*Scheme 2*). However, we isolated from the photo-oxygenation reaction of **1** an additional bicyclic endoperoxide **4** besides indanone and an oxo-indanone-carbaldehyde [5].

Scheme 2

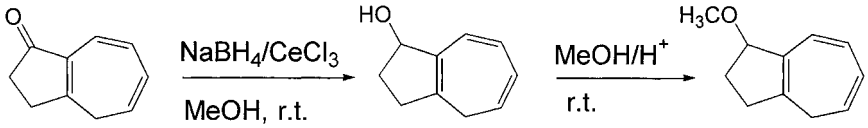


The endoperoxides **2**–**4** derived from the photo-oxygenation of **1** were subjected to thermolysis. To our surprise, the bis-epoxide **5** was formed from the thermolysis of all three endoperoxides **2**–**4**, in addition to the expected *syn*-bis-epoxides **6** and **7** (*Scheme 2*). For the formation of bis-epoxide **5**, we postulated the following reaction mechanism, which involves decomposition of the peroxide linkage by two different

pathways: *a*) cleavage of the O–O bond, which leads to the corresponding *syn*-bis-epoxides by addition of the resulting oxygen radicals to the adjacent C=C bond and *b*) cleavage of the C–O bond as depicted in *Scheme 2*. We assumed that the driving force for the cleavage of the C–O bond is the formation of the oxygen and carbon radicals **8** and **10**, which are stabilized by conjugation with the vinyl and C=O groups. To test the generality of this reaction and shed light on the mechanism of this new endoperoxide-endoperoxide rearrangement, we have synthesized ether derivative **13** where the conjugation of the triene structure in **1** with the C=O group is eliminated. In the following part, we report the photo-oxygenation reaction of **13** and chemical transformations of the bicyclic endoperoxides formed.

Results and Discussion. – The starting material, bicyclic trienone **1**, is a highly functionalized, readily available compound from the diazo ketone of hydrocinnamic acid *via* intramolecular carbene addition [6]. Reduction of trienone **1** with $NaBH_4$ in the presence of $CeCl_3$ in MeOH provided the alcohol **12**, and subsequent treatment with acid in MeOH furnished the corresponding ether **13** in high yield (*Scheme 3*).

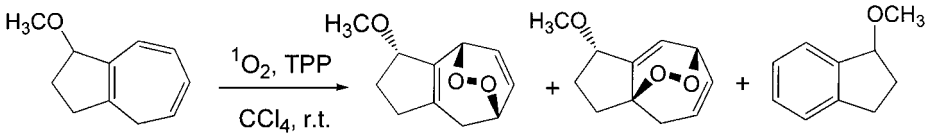
Scheme 3



1 **12** **13**

The photo-oxygenation reaction of **13** in CCl_4 at room temperature was accomplished with tetraphenylporphyrin (TPP) as sensitizer (*Scheme 4*). The ^{1}H-NMR spectrum of the crude material showed that the endoperoxides were formed in addition to the ether **16**. Careful chromatography of the mixture on silica gel provided two bicyclic endoperoxides **14** and **15**, with the *anti*-relation of MeO–C(3) and the peroxide bridge, and the rearranged product **16**.

Scheme 4



13 **14** (48%) **15** (27%) **16** (10%)

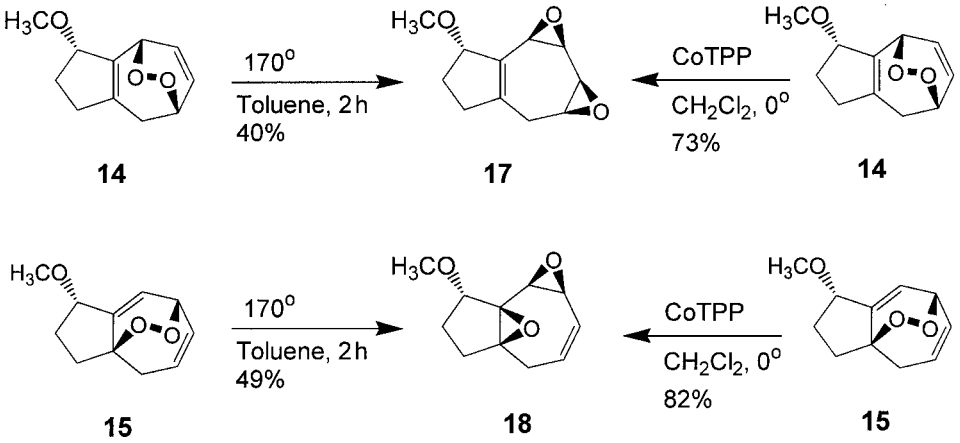
^{1}H- and ^{13}C-NMR spectroscopy, including double-resonance and NOE experiments, allowed the assignment of the proposed structures of the endoperoxides. The *anti*-arrangement was established by ^{1}H-NOE experiments. Irradiation of the resonance line of H–C(1) in **14** ($\delta = 4.85$ ppm) did not induce an enhancement of the signals of the H-atom (H–C(3)), indicating the *anti*-relation of MeO–C(3) and the peroxide bridge. Furthermore, inspection of the *Dreiding* models of **13** shows

clearly that the MeO–C(1) group blocks the *syn*-face of the molecule so that singlet oxygen will attack the triene **13** from the *anti*-face.

It is remarkable that no trace of a (2 + 6) cycloaddition product of type of **4** and (2 + 4) addition products, derived from the valence isomer norcaradiene, were detected among the photo-oxygenation products.

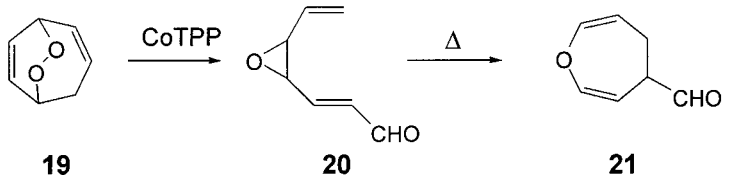
The isolated bicyclic endoperoxides **14** and **15** were then subjected to thermolysis. For this purpose, the endoperoxides were dissolved in toluene and pyrolyzed at 180° in a sealed tube. The thermal stability of the endoperoxides is quite high, and, in both cases, the corresponding bis-epoxides **17** and **18**, respectively, were the only products that were characterized spectroscopically. For chemical characterization of the *syn*-bis-epoxides formed, we have treated **14** and **15** with a catalytic amount of CoTPP [7] at 0° and obtained again the same *syn*-bis-epoxides **17** and **18** as the sole products (*Scheme 5*).

Scheme 5



Earlier, we have shown that the reaction of cycloheptatriene endoperoxide **19** with CoTPP provided the ring-opened aldehyde **20**, involving C–C bond cleavage, besides the expected *syn*-bis-epoxide (*Scheme 6*). Aldehyde **20** could be easily converted to the 4,5-dihydrooxepine-4-carbaldehyde (**21**) [8]. Furthermore, the reaction of some monosubstituted cycloheptatriene [2 + 4] endoperoxides gave similar products [9].

Scheme 6



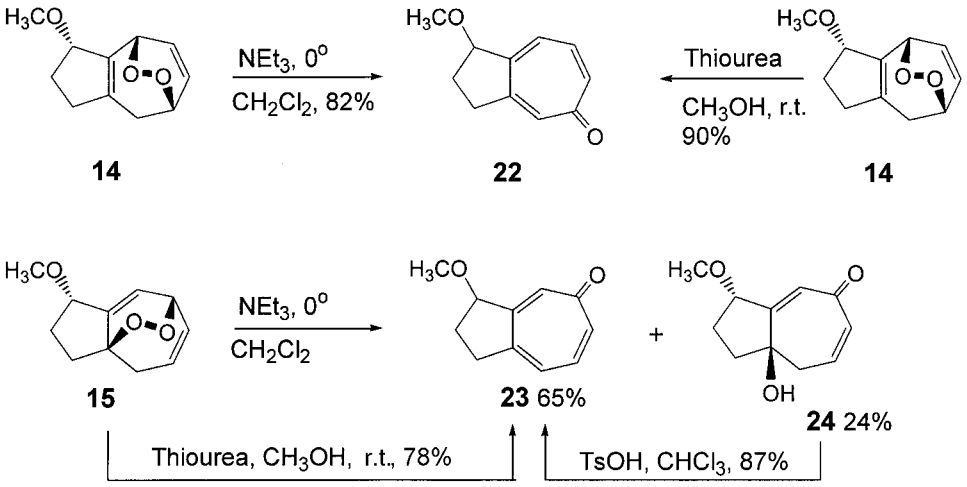
Our mechanistic studies have revealed that the conformational factors in the seven-membered ring formed after cleavage of the O–O bond in the endoperoxides by an electron-transfer mechanism play an important role in determining the product

distribution [8]. Probably, anellation of a five-membered ring in **14** and **15** prevents the molecule from adopting the conformation necessary for the formation of the open-chain aldehydes.

The finding that the bicyclic endoperoxides **14** and **15** do not form even traces of the rearranged bis-epoxide (*Scheme 2*) strongly supports our assumption that the C=O group in **2**–**4** is responsible for this unprecedented endoperoxide-endoperoxide rearrangement.

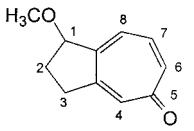
The synthetic potential of endoperoxides is enormous. Base-catalyzed rearrangements of peroxides proceed *via* a general type of β-elimination mechanism to give hydroxy ketones [10]. Application of this reaction to the endoperoxides **14** and **15** should open up an entry to the synthesis of five-membered-ring anellated tropone derivatives.

Scheme 7

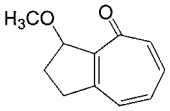


Treatment of the endoperoxides **14** with a catalytic amount of Et_3N at 0° provided the tropone derivative **22** in high yield (*Scheme 7*). Since the peroxide **14** has two different abstractable bridgehead H-atoms, two tropone derivatives **22** and **25** can be formed in the course of the reaction. However, careful analysis of the reaction mixture did not provide any evidence for the formation of the isomer **25** even in traces. Selective formation of **22** indicates that the base abstracts the bridgehead H-atom that is sterically less hindered, and concomitant cleavage of the O–O bond might generate the unsaturated hydroxy ketones, followed by elimination of H_2O to provide **22**. The structural assignment of **22** has been confirmed by differential NOE measurements. Irradiation of the resonance line of H–C(1) in **22** ($\delta = 4.5$ ppm) induces an enhancement of the signals of the olefinic H-atoms (H–C(8)) as well as the signal of one H-atom at C(2), supporting the structure **22**.

The base-catalyzed reaction of the bicyclic endoperoxide **15** resulted in the formation of **23** and the expected product **24**, which is a precursor of **23**. The acid-catalyzed reaction of the hydroxy enone **24** provided tropone **23** in high yield.



22



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Selective reduction of the peroxide linkage with the C=C bond remaining intact can proceed with reagents like $LiAlH_4$ or thiourea [11]. For controlled reduction, thiourea is usually preferred over $LiAlH_4$. We have submitted endoperoxides **14** and **15** to controlled reduction with thiourea. To our surprise, we isolated the corresponding tropone derivatives **22** and **23** in high yields as the sole products. To the best of our knowledge, this is the first case where thiourea acts as a base instead of reducing the peroxide linkages in **14** and **15**.

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Experimental Part

General. M.p.: *Thomas-Hoover* cap. melting-point apparatus. Column chromatography (CC): on silica gel *60* (*Merck*). IR Spectra: *Perkin-Elmer 377* spectrophotometer, from KBr pellets. ^{1}H-NMR: on a 200-MHz *Varian* spectrometer; δ in ppm, Me_4Si as internal standard.

1-Methoxy-1,2,3,4-tetrahydroazulene (**13**): *Method A*. To a magnetically stirred soln. 5 g (34.25 mmol) of *1,2,3,4-tetrahydroazulen-1-one* (**1**) [4] and 3.5 g (14.2 mmol) of solid $CeCl_3$ in 10 ml of MeOH, $NaBH_4$ (1.3 g, 3.38 mmol) was added in small portions at r.t. The mixture was stirred until gas release stopped. To this mixture, 0.1M HCl was added until the color of the mixture became clear. The mixture was stirred for 20 min, diluted with 200 ml of H_2O and extracted 4×50 ml of Et_2O. The Et_2O extracts were combined and dried ($MgSO_4$). After evaporation of solvent, the residue was purified by CC (SiO_2; $CHCl_3$/hexane 1:5): **13** (4.5 g, 81%). Yellow liquid. IR (KBr): 3029*m*, 3000*s*, 2953*m*, 2800*s*, 1150*s*, 770*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.58 (*d*, *A* of *AB*, ^3J = 11.0, H–C(8)); 6.43 (*dd*, *B* of *AB*, $^3J = 11.0$, $^3J = 5.3$, H–C(7)); 6.06 (*dd*, *A* of *AB*, $^3J = 9.9$, $^3J = 5.3$, H–C(6)); 5.53 (*dt*, *B* of *AB*, $^3J = 9.9$, $^3J = 6.6$, H–C(5)); 4.45 (*m*, H–C(1)); 3.28 (*s*, MeO); 2.45 (*m*, 2 H); 2.22 (*m*, 1 H); 1.96 (*m*, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 139.80; 135.90; 129.88; 128.03; 127.90; 121.74; 86.98 (C(1)); 55.88 (MeO); 35.12; 30.20; 29.17. Anal. calc. for $C_{11}H_{14}O$: C 81.44, H 8.70; found: C 81.42, H 8.55.

Method B. A suspension of 1 g (26.3 mmol) of $LiAlH_4$ in 10 ml of dry THF was added dropwise with stirring to 5 g (34.25 mmol) of **1** in 50 ml of dry THF under N_2 at 0°. After 1 h, the mixture was quenched by the dropwise addition of 50 ml of 50% aq. THF. The mixture was diluted with H_2O and extracted with 4×50 ml Et_2O. The Et_2O extracts were combined, dried ($MgSO_4$), and evaporated. Crude product **12** was dissolved in 100 ml of MeOH, and 5 ml of 0.1M HCl was added, and the mixture was stirred at r.t. After 2 h, the mixture was diluted with 90 ml of H_2O and extracted with 4×50 ml Et_2O. The Et_2O extracts were combined, dried ($MgSO_4$), and concentrated to give 3.9 g (72%) of **13** as a yellow oil.

Photo-oxygenation of **13**. A soln. of 3 g (18.52 mmol) of **13** and 50 mg tetraphenylporphyrin (TPP) in 100 ml of CCl_4 was irradiated with a projector lamp (150 W), while a slow stream of dry O_2 was passed through it continuously. The progress of the photo-oxygenation was monitored by ^{1}H-NMR spectroscopy until consumption of the starting material was essentially complete (8 h). The solvent was evaporated at r.t. CC of the crude product (silica gel, AcOEt/hexane 15:85) yielded the bicyclic endoperoxides **14**, **15**, and *2,3-dihydro-1-methoxy-1*H*-indene* (**16**). The first fraction contained **16** (274 mg 10%). From the second fraction, we isolated anti-*4-methoxy-11,12-dioxatricyclo[5.3.2.0^{1,5}]dodeca-5,8-diene* (**15**; 970 mg, 27%). Colorless liquid. IR (KBr): 3100*m*, 3055*m*, 3000*s*, 2953*m*, 2875*m*, 1472*w*, 1260*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.76 (*d*, $^3J = 7.0$, H–C(6)); 6.10 (*m*, H–C(8)); 5.70 (*dt*, H–C(9)); 4.67 (*t*, $^3J = 6.9$, H–C(7)); 4.21 (*m*, H–C(4′)); 3.26 (*s*, MeO); 2.87 (*ddd*, *A* of *AB*, $^2J = 15.8$, $^3J = 6.0$, $^4J = 2.3$, 1 H–C(10)); 2.31 (*ddd*, *B* of *AB*, $^2J = 15.8$, 1 H–C(10)); 1.84–2.01 (*m*, 2 H–C(2), 2 H–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 144.13; 131.46; 129.28; 129.22; 87.15; 83.30; 72.92; 56.20; 42.58; 37.07; 31.11. Anal. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 68.33, H 7.14.

From the third fraction, we isolated anti-*3-methoxy-9,10-dioxatricyclo[6.2.2.0^{2,6}]dodeca-2(6),11-diene* (**14**; 1720 mg, 48%). Pale yellow liquid. IR (KBr): 3150*w*, 3080*w*, 3000*s*, 2953*s*, 2875*s*, 1430*m*, 1260*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.78 (*dd*, *A* of *AB*, $^3J = 8.3$, $^3J = 7.2$, H–C(11)); 6.33 (*t*, *B* of *AB*, $^3J = 8.3$, H–C(12)); 4.81–4.89 (*m*, H–C(1), H–C(8)); 4.55 (*m*, H–C(3)); 3.31 (*s*, MeO); 2.78–2.93 (br. *d*, 1 H–C(7)); 1.83–2.41 (*m*, 2 H–C(4), 2 H–C(5), 1 H–C(7)). ^{13}C-NMR (50 MHz, $CDCl_3$): 143.16; 137.62; 135.24; 125.47; 88.32; 76.86; 73.28; 56.27; 36.39; 34.91; 28.58. Anal. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 67.88, H 7.11.

Thermolysis of **14**. A soln. of **14** (500 mg, 2.57 mmol) in toluene (5 ml) sealed *in vacuo* in a constricted test tube was heated in an oil bath for 2 h at 180°. After cooling to r.t., the mixture was evaporated. The thermolysate was submitted to TLC (silica gel; AcOEt/hexane 25:75): 200 mg (40%) of *(1a*SR,*1b*RS,*2a*RS,*6*RS,*6b*SR*)-6-methoxy-1a,1b,2a,3,4,5,6,6b-octahydroazuleno[4,5-*b*:6,7-*b*]bisoxirene* (**17**), as a colorless oil. IR (KBr, film): 3000*m*, 2953*s*, 2875*m*, 1870*m*, 1472*m*, 1242*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.53 (*m*, H–C(6)); 3.62 (*m*, 2 CH–O); 3.30 (*s*, MeO); 2.83 (*m*, 2 CH–O); 2.8–1.84 (*m*, 3 CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 142.93; 131.50; 88.60; 56.57; 53.34; 52.69; 51.77; 50.89; 37.17; 29.10; 27.62. Anal. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 67.75, H 7.08.

Thermolysis of **15**. Compound **15** (520 mg, 2.68 mmol) was thermolyzed as described above: bis-epoxide **18** (255 mg, 49%). Colorless oil. IR (KBr): 3000*m*, 2953*s*, 2875*m*, 1870*m*, 1472*m*, 1242*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.78 (br. *s*, CH=CH); 4.08 (*d*, $^3J = 5.3$, 1 H); 3.75 (*d*, *A* of *AB*, $^3J = 3.9$, CH–O); 3.48 (*m*, *B* of *AB*, CH–O); 3.35 (*s*, MeO); 2.91 (*dd*, *A* of *AB*, $^2J = 15.4$, $^3J = 4.0$, 1 H, CH_2); 2.62 (*dd*, *B* of *AB*, $^2J = 15.4$, $^2J = 5.9$, 1 H, CH_2); 1.51–1.92 (*m*, 2 CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 130.25; 125.56; 83.79; 66.38; 64.98; 57.83; 54.13; 52.88; 30.69; 27.89; 25.96. Anal. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 68.26, H 7.11.

CoTPP-Catalyzed Reaction of **14**. To a magnetically stirred soln. of **14** (300 mg, 1.55 mmol) in CH_2Cl_2 (25 ml) was added a soln. of *meso*-tetraphenylporphyrin-Co^{II} (50 mg, 0.1 mmol) in CH_2Cl_2 (20 ml) at 0°. After complete addition (15 min), the mixture was stirred 20 min at r.t. and then evaporated. TLC (silica gel; AcOEt/hexane 25:75) gave **17** (220 mg, 73%).

CoTPP-Catalyzed Reaction of **15**. Compound **15** (330 mg, 1.70 mmol) was reacted with *meso*-tetraphenylporphyrin-Co^{II} as described above: **18** (270 mg, 82%).

Et_3N-Catalyzed Rearrangement of **14**. A soln. of **14** (420 mg, 2.16 mmol) and Et_3N (220 mg, 2.18 mmol) in 50 ml of CH_2Cl_2 was stirred at 0° for 12 h. After evaporation of the solvent, the residue was submitted to CC (silica gel; $CHCl_3$/MeOH 99:1) to give *1-methoxy-1,2,3,5-tetrahydroazulen-5-one* (**22**; 330 mg, 87%). Colorless liquid. IR (KBr, film): 3000*w*, 2953*m*, 1620*m*, 1600*s*, 1240*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.91–7.13 (*m*, 4 arom. H); 4.45 (*t*, H–C(1)); 3.42 (*s*, MeO); 2.64–3.03 (*m*, 2 H–C(3)); 2.35 (*m*, 1 H–C(2)); 1.85 (*m*, 1 H–C(2)). ^{13}C-NMR (50 MHz, $CDCl_3$): 180.60; 154.58; 153.40; 143.66; 143.66; 139.21; 137.51; 131.51; 87.23; 58.70; 34.98; 32.89. Anal. calc. for $C_{11}H_{12}O_2$: C 74.98, H 6.86; found: C 75.13, H 6.73.

Thiourea Reaction of **14**. To a magnetically stirred slurry of (160 mg, 2.1 mmol) of thiourea in 5 ml of MeOH was added a soln. of (410 mg, 2.11 mmol) of **14** in 20 ml of MeOH at r.t. After complete addition, the mixture was stirred for 2 h, the solids were removed by filtration, MeOH was evaporated, and the residue purified by TLC (silica gel; $CHCl_3$/MeOH 99:1) affording pure **22** (335 mg, 90%).

Et_3N-Catalyzed Rearrangement of **15**. Endoperoxide **15** (620 mg, 3.2 mmol) was reacted with Et_3N as described above. The CC of the residue (silica gel; $CHCl_3$/MeOH 99:1) gave as the first fraction *3-methoxy-1,2,3,5-tetrahydroazulen-5-one* (**23**; 403 mg, 65%). Colorless liquid. IR (KBr, film): 3005*w*, 2960*m*, 2830*w*, 1618*m*, 1600*s*, 1230*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.1 (br. *s*, 1 arom. H); 7.06–6.85 (*m*, 3 arom. H); 4.42 (*dt*, $^3J = 6.3$, $^2J = 1.2$, H–C(3)); 3.45 (*s*, MeO); 2.91 (*m*, 1 H–C(1)); 2.75 (*m*, 1 H–C(1)); 2.24 (*m*, 1 H–C(2)); 1.92 (*m*, 1 H–C(2)). ^{13}C-NMR ($CDCl_3$): 188.91; 154.78; 153.69; 142.35; 139.43; 138.12; 131.28; 87.62; 58.85; 34.49; 32.98. Anal. calc. for $C_{11}H_{12}O_2$: C 74.98, H 6.86; found: C 74.73, H 6.91.

As the second fraction, *(3*RS,*8a*SR*)-8a-hydroxy-3-methoxy-2,3,8,8a-tetrahydroazulen-5(1*H*)-one* (**24**; 149 mg, 24%) was isolated. Colorless liquid. IR (KBr, film): 3400*s*, 3000*w*, 1700*m*, 1620*m*, 1240*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.43 (*ddd*, $^3J = 12.7$, 7.3 and, 2.9, H–C(7)); 6.21 (*m*, 2 H–C(6), H–C(4)); 4.22 (*t*, H–C(3)); 3.4 (*s*, MeO); 2.65–3.10 (*m*, 2 H–C(8)); 1.85–2.10 (*m*, 2 H–C(1), 2 H–C(2)). ^{13}C-NMR ($CDCl_3$): 191.48; 161.49; 140.54; 133.51; 128.70; 84.06; 77.52; 57.32; 41.23; 39.40; 29.64. Anal. calc. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 67.88, H 7.11.

TsOH-Catalyzed Reaction of **24**. Compound **24** (149 mg, 0.77 mmol) was dissolved in 20 ml of $CHCl_3$, and 20 mg (0.12 mmol) of solid TsOH was added. The resulting soln. was refluxed for 12 h. The mixture was cooled and washed with $NaHCO_3$ soln. and dried ($MgSO_4$). Evaporation of the solvent gave **23** (120 mg, 87%).

Thiourea Reaction of **15**. To a magnetically stirred slurry of thiourea (160 mg, 2.1 mmol) in 5 ml of MeOH was added a soln. of **15** (480 mg, 2.5 mmol) in 20 ml of MeOH at r.t. After complete addition, the mixture was

stirred for 2 h, the solids were removed by filtration, the MeOH was evaporated, and the residue purified by TLC (silica gel; $CHCl_3$/MeOH 99:1): pure **23** (340 mg, 78%).

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