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Rhenium and Ruthenium Induced Ring Closing Olefin Metathesis to Hydroazulenes

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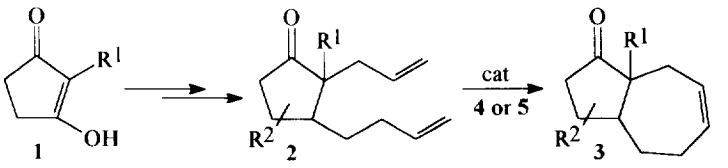
Abstract: *Several highly functionalized diolefins cyclize to hydroazulenes via olefin metathesis catalyzed either by CH_3ReO_3[1] or by the ruthenium catalyst synthesized by Grubbs.[2] We demonstrate the superiority of the ruthenium catalyst.*

INTRODUCTION

Olefin metathesis offers an attractive possibility to carry out C-C bond formation with non-activated double bonds.[3] Especially interesting are selective ring closing reactions in the presence of other functionalities. In the course of our efforts to apply olefin metathesis to natural product synthesis, we became interested in seven membered ring cyclizations to obtain hydroazulenes.

Starting from 1,3-cyclopentanedione derivatives **1**, different hydroazulene precursors of type 2 are easily obtained by standard reactions such as the vinylogous ester trick, α-alkylation and Birch reduction. It should, in principle, be possible to synthesize hydroazulenes **3** from precursors of type **2** by olefin metathesis.

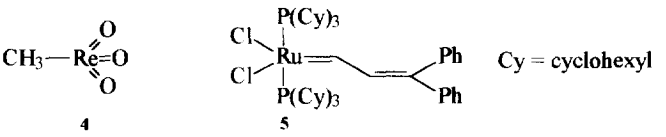


R^1 = H, CH_3

R^2 = H, CH_3, cyclopropane, epoxide, olefin

Scheme 1.

Recently, we have demonstrated this new approach towards hydroazulenes with a few examples. We described ring closing reactions using the heterogeneous catalyst system methyltrioxorhenium (MTO) **4** on silica gel/aluminium oxide as a carrier.[4] In the course of our studies the limited scope of catalyst **4** and the advantages of the homogeneous ruthenium catalyst **5** for the transformation of **2** → **3** were recognized, as we report herein.

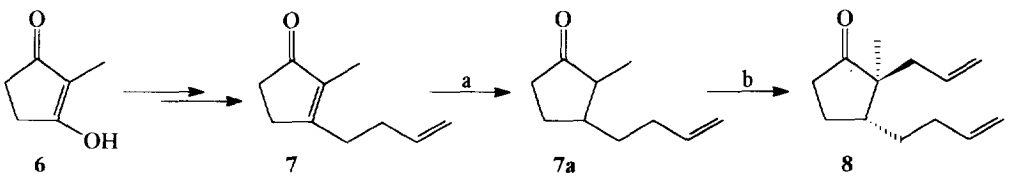


Scheme 2. Catalysts for olefin metathesis.

Natural products of hydroazulene type **3** have either *cis* or *trans* anellation.[5] Therefore, we have investigated the cyclization behaviour of different substituted cyclopentanone derivatives **2**, which contain either *cis* or *trans* connected allyl and homoallyl side chains. The hydroazulenes and the precursors were synthesized in racemic form.

SYNTHESIS

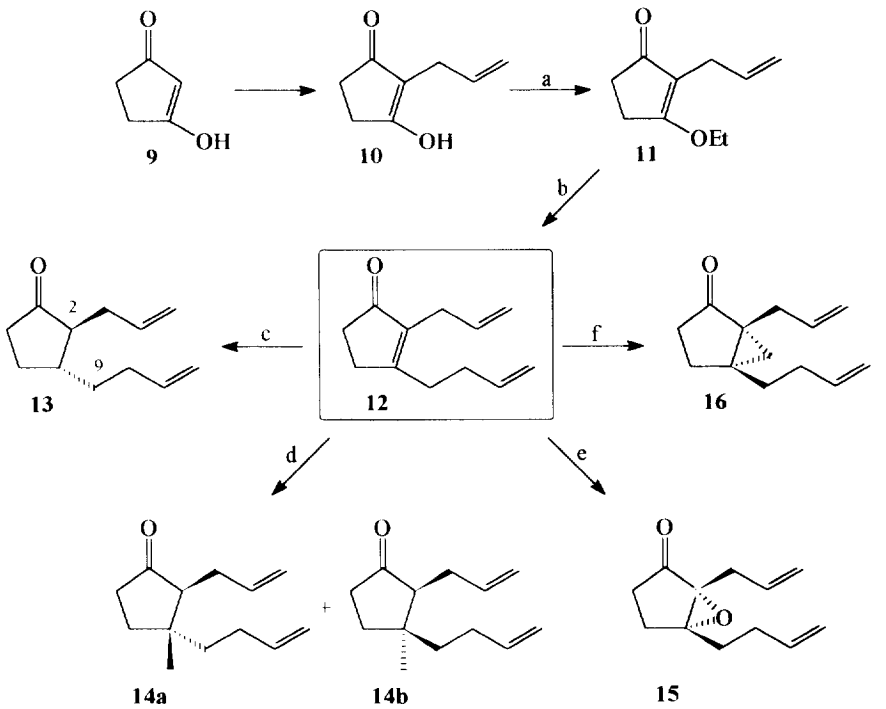
Hydroazulene precursor **8** was synthesized from 2-methyl-1,3-cyclopentanedione (**6**). In two steps 3-but-3-enyl-2-methyl-2-cyclopentenone (**7**) was obtained.[6] Birch reduction of ketone **7** gave 3-but-3-enyl-2-methyl-cyclopentanone (**7a**) in good yield. The allylic side chain in **8** was introduced by alkylation of the cyclopentanone **7a** with allyl bromide and potassium hydride in THF, giving rise to 2-allyl-3-but-3-enyl-2-methyl-cyclopentanone (**8**) in moderate yield.



Scheme 3. Reaction conditions. a) 1. aq. NH_3, Li, *t*-BuOH, THF; 2. H_2O, 69%; b) KH, CH_2=$CHCH_2Br$, THF, 25%.

The synthesis of six other hydroazulene precursors has been investigated. The first step of the synthesis was the alkylation of cyclopentane-1,3-dione (**9**) to obtain **10**.[7] Etherification of **10** gave the vinylogous ester **11** in excellent yield. Grignard reaction and acidic workup led to 2-allyl-3-but-3-enyl-2-cyclopentenone (**12**) which is a useful intermediate for other derivatives.The hydroazulene precursors **13**, **14a**, **14b**, **15** and **16** were each synthesized respectively, from **12** in only one step.

2-Allyl-3-but-3-enyl-cyclopentanone **(13)** was easily obtained by Birch reduction under the same conditions as described above for compound **7a**. The stereochemistry of **13** was assigned by NOE effects between the proton signals of the methine proton H-2 and the methylene proton H-9. 2-Allyl-3-but-3enyl-3-methyl-cyclopentanone **(14)** was obtained in moderate yield by reaction of **12** with three equivalents of methylcopper and boron trifluoride etherate in ether, 52% starting material was recovered.[8] The resultant product consisted of the two diastereomeric forms **14a** and **14b** in the ratio of 1.5 to 1.0 as determined by ^{1}H NMR.[9] The proton signal of the angular methyl group from **14a** is at 0.85 ppm and the signal from **14b** is at 1.14 ppm. 1-Allyl-5-but-3-enyl-6-oxa-bicyclo[3.1.0]hexan-2-one **(15)** was obtained in 63% yield by treatment of **12** with H_2O_2 and NaOH in MeOH.[10] The cyclopropane ring was introduced into **12** with trimethyloxosulfonium iodide to gave rise to 1-allyl-5-but-3-enyl-bicyclo[3.1.0]hexan-2-one **(16)**.[11]



Scheme 4. Reaction conditions. a) EtOH, benzene, *p*-TsOH, 96%; b) 1. CH_2=$CHCH_2CH_2MgBr$, Et_2O; 2. H_3O^+, 49%; c) 1. aq. NH_3, Li, *t*-BuOH, THF; 2. H_2O, 66%; d) 3 eq. MeLiCuI, BF_3Et_2O, Et_2O, 18% + 52% starting material; e) H_2O_2, NaOH, MeOH, 63%; f) $(CH_3)_3S(=O)I$, NaH, DMSO, 33%.

The ring closing olefin metathesis leading to different substituted hydroazulenes is depicted in scheme 5. It is demonstrated that methyltrioxorhenium can cyclize precursor **13** to the *trans* anellated hydroazulene **17** in good yield. The stereochemistry of **17** was assigned by NOE effects between the proton signals of the methine proton H-8a and the methylene proton H-4. The reaction was carried out in 1,1,2-trichlorotrifluoroethane (TTE), with finely ground STREM carrier (87% SiO_2; 13% Al_2O_3) under argon atmosphere. The best results were obtained by heating under reflux for several days. This represents a new approach towards *trans* anellated hydroazulenes.

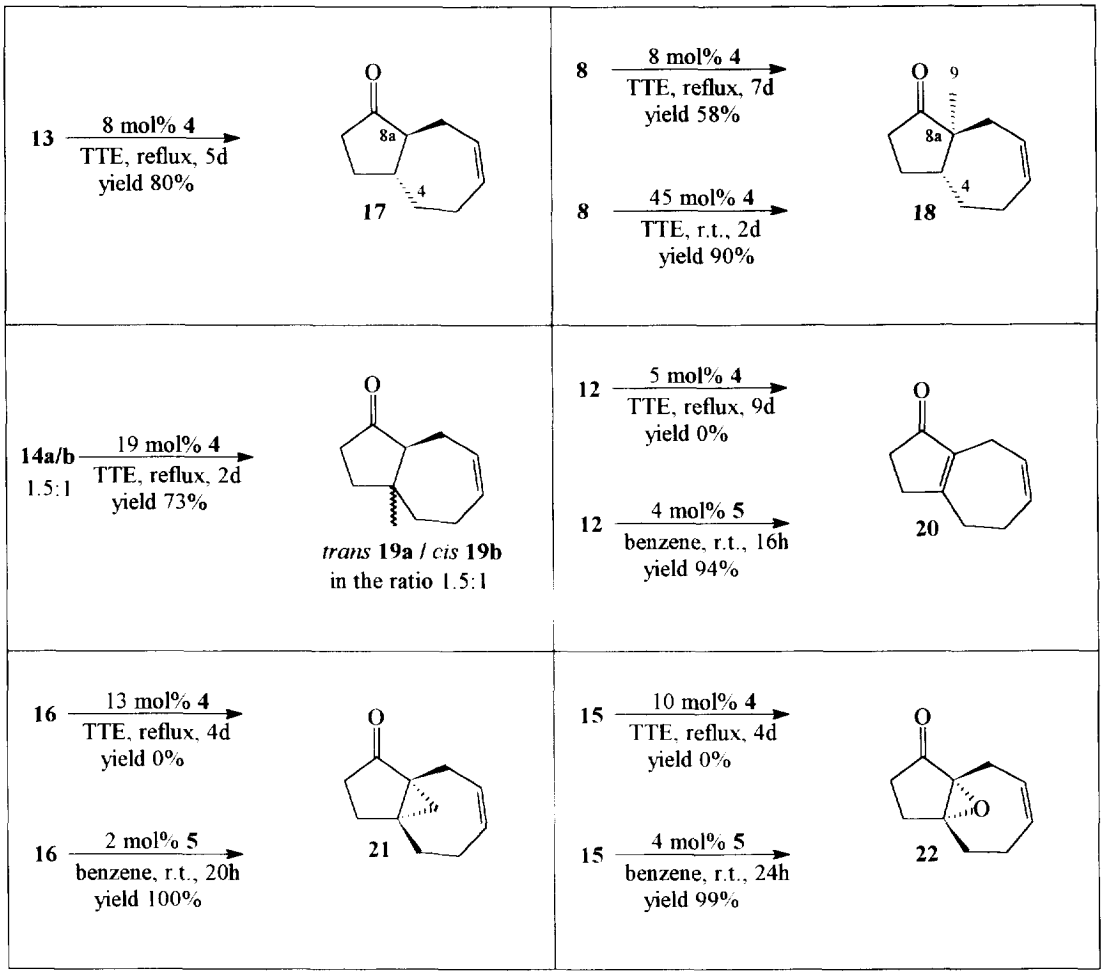
We were interested how ring closing olefin metathesis is influenced by steric and stereochemical effects. Therefore, we synthesized **8** which contains a quaternary centre. The methyl group also causes greater steric hindrance. Nevertheless, the olefin metathesis using methyltrioxorhenium resulted the hydroazulene **18**. The *trans* stereochemistry was confirmed by NOE effects between the proton signals of the angular methyl group (H-9) at C-8a and the methylene proton H-4. It is noted, that the yield of **18** was significantly lower under the same reaction conditions as employed in the synthesis of **17**. Heating under reflux with 8 mol% methyltrioxorhenium yielded 58% **18**. To improve the yield large amounts (45 mol%) of catalyst were required. In this case the reaction was carried out at room temperature.

In the ring closing olefin metathesis of **14a/14b** (ratio of diastereomers 1.5:1.0) the two diastereomeric hydroazulenes **19a** and **19b** were also obtained in good yield. The ratio of diastereomers remained unchanged. The stereochemistry of **19a** and **19b** was assigned by ^1H NMR.[9] The proton signal of the angular methyl group from **19a** is at 0.85 ppm and the signal from **19b** is at 1.18 ppm. A separation of **19a** and **19b** was impossible. The synthesis of hydroazulene **19b** demonstrated, that methyltrioxorhenium is also able to build *cis* anellated ring systems. The unchanged ratio of diastereomers suggested that the *cis* or *trans* connected side chains, in the case of **14a/14b**, do not influence the metathesis reaction.

After this successful ring closing olefin metathesis with methyltrioxorhenium, which is described above, compounds containing other functionalities as well as high ring strains were to be tested for olefin metathesis. The precursors **12**, **15** and **16** were synthesized. But olefin metathesis with methyltrioxorhenium failed. In the case of **12** and **16** only starting material was isolated. The epoxide **15** decomposed under the reaction conditions required for methyltrioxorhenium. These negative results limit the use of methyltrioxorhenium.

In contrast, the ruthenium catalyst was able to cyclize **12**, **15** and **16** in nearly quantitative yield. The reactions were carried out in benzene under argon (glove box). The ring closing reactions took place at room temperature. Reaction times were in the range of 16 to 24 hours. The reactions were monitored by GC/MS. Only 2 to 4 mol% ruthenium catalyst was necessary.

The successful cyclization of **12** to **20** shows, that an α,β-unsaturated carbonyl group in neighbourhood of the reaction centres does not affect the metathesis reaction. Up to now it was only known that an α,β-unsaturated ester at a large distance from the reaction centres does not interfere with ring closing olefin metathesis.[12]



Scheme 5. Synthesis of hydroazulenes by ring closing olefin metathesis.

The olefin metathesis of **16** with the ruthenium catalyst yielding **21** led to a highly strained tricyclic ring system. This demonstrated, that the ruthenium catalyst is able to build ring systems, which are otherwise difficult to generate.

Compound **20** with one electron-deficient and one electron-rich double bond, which can be differentiated easily, should be a useful intermediate for the synthesis of natural products of the hydroazulene type. The same holds for **21**.

Even hydroazulene **22** was obtained in nearly quantitative yield using the ruthenium catalyst. An attack on the epoxide could open an approach to a *trans* diol as well as to other hydroazulenes, which have functional groups at the α- and β-position to the carbonyl group. This structure element is often incorporated in natural products of the hydroazulene type.[5]

Otherwise hardly available compounds - for example hydroazulene **22** - were easily obtained under mild conditions (r.t.) and with excellent yield (99%) using the ruthenium catalyst. This demonstrates once more impressively the new possibilities offered by ring closing olefin metathesis.

CONCLUSION

We are able to show that ring closing olefin metathesis is very useful for the preparation of a wide range of substituted hydroazulenes.The limited applicability of methyltrioxorhenium is demonstrated. We show that the ruthenium catalyst is able to build strained ring systems. Even an α,β-unsaturated carbonyl group in the neighbourhood of the reaction centres is accepted by the ruthenium catalyst. The high tolerance of olefin metathesis towards functional groups should allow new synthetic routes to natural products. Further investigations in this field like f. i. the synthesis of sesquiterpenes with the hydroazulene skeleton are currently under investigation in our laboratories.

EXPERIMENTAL

General

^{1}H NMR spectra were obtained using the Bruker AC 200 (200 MHz) and AM 400 (400 MHz) instruments with $CDCl_3$ (δ = 7.26 ppm) as an internal standard. Coupling constants were measured in Hertz. ^{13}C NMR spectra were measured with the Bruker AC 200 (50.32 MHz), AM 270 (67.93 MHz) and AM 400 (100.64 MHz) instruments. The IR spectra were recorded on the Perkin-Elmer 157G and 881 spectrometers, either in $CHCl_3$ or CCl_4. The solvent is mentioned. Mass spectra were run on a Varian MAT 711 at 70 eV. GC/MS spectra were recorded on a Hewlett-Packard GC HP 5890II connected with a MS HP 5971A. Reactions under inert conditions were carried out in a MBRAUN glove box MB 120 G. Baker flash silica gel (0.03-0.06 mm) was used for flash liquid chromatographic purification. Diethyl ether was distilled from sodium wire, tetrahydrofuran was distilled from potassium, dichloromethane and 1,1,2-trichlorotrifluoroethane were distilled from calcium hydride and dry benzene was obtained from Merck or Aldrich.

3-But-3-enyl-2-methyl-cyclopentanone (7a)

357 mg (51 mmol) lithium were added to 100 ml liquid ammonia at -78°C. After stirring the solution for 30 min 763 mg (5.09 mmol) 3-but-3-enyl-2-methyl-2-cyclopentenone (**7**) and 1.85 g *tert*-butanol, dissolved in 15 ml Et_2O, were added at -78°C. Stirring was continued for a further 100 min at this temperature. Then 50 ml water

were carefully added to the cold mixture. The reaction mixture was warmed up, so the ammonia evaporated. MTBE was added and the phases were separated. The organic layer was washed with 5% HCl, saturated sodium bicarbonate solution, water and brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:20) to give a colourless oil (69%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.83 (1H, ddt, J = 17 Hz, 10.5 Hz, 6.5 Hz), 5.05 (1H, dm, J = 17 Hz), 4.98 (1H, dm, J = 10.5 Hz), 2.37 (1H, dd, J = 18 Hz, 9 Hz), 2.28-1.11 (9H, m), 1.07 (80% 3H, d), 0.97 (20% 3H, d) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz): δ = 221.1 (C), 138.4 (CH), 114.7 (CH_2), 50.4 (CH), 44.1 (CH), 37.3 (CH_2), 33.6 (CH_2), 31.3 (CH_2), 27.0 (CH_2), 12.5 (CH_3) ppm. IR ($CHCl_3$): ν = 3016, 1732, 1262, 1014 cm^{-1}. MS: m/z (%) = 152 (21, M^+), 110 (76), 95 (52), 81 (63), 67 (52), 55 (100). HRMS calcd. for $C_{10}H_{16}O$ (M^+) 152.1201 found 152.1201.

2-Allyl-3-but-3-enyl-2-methyl-cyclopentenone (8)

To 40 mg (1 mmol) potassium hydride a solution of 152 mg 3-but-3-enyl-2-methyl-cyclopentanone (**7a**) in 5 ml abs.THF was added. After stirring 40 min at room temperature 145 mg (1.2 mmol) allyl bromide in 5 ml abs. THF were added. After 2 h the reaction was quenched with brine. The aqueous phase was extracted with MTBE. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:20) to give a colourless oil (25%). ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.84-5.62 (2H, m), 5.11-4.94 (4H, m), 2.45 (1H, dd, J = 14 Hz, 6.5 Hz), 2.08 (1H, dd, J = 18 Hz, 9.5 Hz), 2.01 (1H, dd, J = 14 Hz, 8.5 Hz), 2.01 (1H, m), 1.95-1.20 (4H, m), 1.08-0.86 (3H, m), 0.68 (3H, s) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz): δ = 223.1 (C), 138.5 (CH), 134.2 (CH), 118.0 (CH_2), 114.7 (CH_2), 51.2 (C), 41.8 (CH), 40,3 (CH_2) 37.3 (CH_2), 31.7 (CH_2), 28.9 (CH_2), 24.7 (CH_2), 17.5(CH_3) ppm. IR ($CHCl_3$): ν = 3013, 2969, 1731, 1232, 997, 918 cm^{-1}. MS: m/z (%) = 192 (13, M^+), 149 (41), 137 (46), 109 (79), 95 (93), 55 (100). HRMS calcd. for $C_{13}H_{20}O$ (M^+) 192.1514 found 192.1514.

2-Allyl-3-ethoxy-2-cyclopentenone (11)

4 g (29 mmol) 2-allyl-1,3-cyclopentanedione (**10**), 0.2 g *p*-toluenesulfonic acid, 40 ml ethanol and 20 ml benzene were combined and heated under reflux for 30 h. A dropping funnel containing activated molecular sieves (4 Angström) was installed between flask and condenser to remove the reaction water. After cooling, the solvent was evaporated under reduced pressure. The crude product was purified by kugelrohr distillation at 0.1 mbar and 100°C to give a colourless oil (96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.82 (1H, ddt, J = 17 Hz, 10 Hz, 6.5 Hz), 5.00 (1H, dm, J = 17 Hz), 4.94 (1H, dm, J = 10 Hz), 4.22 (2H, q, J = 7 Hz), 2.89 (2H, d, J = 6 Hz), 2.66 (2H, m), 1.39 (3H, t, J = 7 Hz) ppm. IR ($CHCl_3$): ν = 3011, 1682, 1379, 1352, 1259, 1237 cm^{-1}. MS: m/z (%) = 166 (100, M^+), 152 (66), 137 (86), 123 (64), 95 (85), 81 (57), 67 (45). HRMS calcd. for $C_{10}H_{14}O_2$ (M^+) 166.0994 found 166.0998.

2-Allyl-3-but-3-enyl-2-cyclopentenone (12)

A solution of 4-bromo-1-butene 6.75 g (50 mmol) in 20 ml abs. Et_2O was added slowly to a stirred solution of 1.4 g (58 mmol) of magnesium turnings in 40 ml abs. Et_2O. It was heated under gentle reflux for 30 min. After cooling to 0°C 4.6 g (27.6 mmol) 2-allyl-3-ethoxy-2-cyclopentenone **(11)**, dissolved in 10 ml abs. Et_2O, were added. It was stirred for 2 h at room temperature. The reaction was quenched with water. The reaction mixture was acidified carefully with 5% HCl to pH 2. The phases were separated and the aqueous phase was extracted with MTBE. The combined organic layers were washed with a saturated solution of $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:4) to give a yellow oil (49%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.80 (2H, m), 5.02 (4H, m), 2.94 (2H, d, J = 6 Hz), 2.53 (4H, m), 2.39 (2H, m), 2.31 (2H, m) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz): δ = 209.0 (C), 174.0 (C), 138.1 (C), 136.9 (CH), 134.7 (CH), 115.5 (CH_2), 115.1 (CH_2), 34.0 (CH_2), 31.1 (CH_2), 30.3 (CH_2), 29.1 (CH_2), 27.1 (CH_2) ppm. IR ($CHCl_3$): ν = 1691, 1638 cm^{-1}. MS: m/z (%) = 176 (54, M^+), 135 (85), 105 (49), 93 (100), 91 (99), 79 (64), 77 (63). HRMS calcd. for $C_{12}H_{16}O$ (M^+) 176.1201 found 176.1201.

2-Allyl-3-but-3-enyl-cyclopentanone (13)

70 mg (10 mmol) lithium were added to 30 ml liquid ammonia at -60°C. After stirring for 15 min 176 mg (1 mmol) 2-allyl-3-but-3-enyl-2-cyclopentenone **(12)** and 370 mg (5 mmol) *tert*-butanol, dissolved in 2 ml THF, were added at -60°C. It was stirred for 45 min at the same temperature. Then 20 ml water were carefully added at -60°C. The reaction mixture was warmed up, so the ammonia evaporated. MTBE was added and the phases were separated. The aqueous phase was extracted with MTBE.The combined organic layers were washed with 5% HCl and brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:20) to give a colourless oil (66%). The stereochemistry was assigned by NOE. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.78 (2H, m), 5.02 (4H, m), 2.41 (1H, m), 2.30 (1H, m), 2.00 (2H, m), 1.87 (1H, m), 1.76-1.50 (4H, m), 1.47 (1H, m), 1.02 (1H, m), 0.84 (1H, m) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz): δ = 220.0 (C), 138.3 (CH), 135.3 (CH), 116.9 (CH_2), 114.7 (CH_2), 54.5 (CH), 40.3 (CH), 37.8 (CH_2), 33.6 (CH_2), 32.1 (CH_2), 31.1 (CH_2), 26.8 (CH_2) ppm. IR ($CHCl_3$): ν = 1736, 918 cm^{-1}. MS: m/z (%) = 178 (36, M^+), 149 (44), 136 (48), 123 (76), 95 (93), 79 (100). HRMS calcd. for $C_{12}H_{18}O$ (M^+) 178.1358 found 178.1357.

2-Allyl-3-but-enyl-3-methyl-cyclopentanone (14a) + (14b)

Under an argon atmosphere 10 ml abs. Et_2O was added to 972 mg (5.1 mmol) anhydrous copper(I)iodide. A solution of 112 mg (5.1 mmol) methyl lithium in Et_2O was added dropwise at -35°C. After stirring for 5 min 724 mg (5.1 mmol) BF_3OEt_2 were added slowly at -75°C. After 5 min a solution of 900 mg (5.1 mmol) **12** in 10 ml abs. Et_2O was added at -75°C. Within 20 h the solution was allowed to warm up slowly to -5°C. Then the reaction mixture was quenched with water. MTBE was added and the phases were separated. The aqueous

phase was extracted with MTBE. The combined organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:4) to give a colourless oil (18%, 58 mg, 0.32 mmol). 52% starting material was recovered Two diastereomers were isolated in a ratio of 1.5 (**14a**) to 1.0 (**14b**), assigned by ^{1}H NMR.. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.99-5.72 (2H, m), 5.11-4.89 (4H, m), 2.46-1.08 (11H, m), 1.14 (40% 3H, s), 0.85 (60% 3H, s) ppm. IR ($CHCl_3$): ν = 1732 cm^{-1}. MS: m/z (%) = 192 (6, M^+), 177 (14), 175 (9), 163 (6), 149 (11), 137 (38), 135 (39), 109 (20); 107 (20), 96 (100), 95 (63), 81 (43), 79 (44), 67 (63), 55 (91). HRMS calcd. for $C_{13}H_{20}O$ (M^+) 192.1514 found 192.1514.

1-Allyl-3-but-3-enyl-6-oxa-bicyclo[3.1.0]hexan-2-one (15)

To a solution of 44 mg (0.25 mmol) **12** in 2 ml methanol two drops of a 30% solution of hydrogen peroxide and one drop of a 5% solution of NaOH were added. After stirring for 2 h at room temperature 5 ml water were added. The aqueous layer was extracted with MTBE. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:10) to give a colourless oil (63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.84 (2H, m), 5.08 (4H, m), 2.63 (1H, dd, J = 15 Hz, 6.5 Hz), 2.40 (1H, ddm, J = 15 Hz, 6.5 Hz), 2.30 (4H, m), 2.09 (1H, m); 1.98- 1.80 (3H, m) ppm. IR ($CHCl_3$): ν = 1741, 921 cm^{-1}. MS: m/z (%) = 192 (4, M^+), 151 (12), 123 (25), 95 (28), 85 (63), 83 (100), 81 (48). HRMS calcd. for $C_{12}H_{16}O_2$ (M^+) 192.1150 found 192.1150.

1-Allyl-5-but-3-enyl-bicyclo[3.1.0]hexan-2-one (16)

To a solution of 15 mg (0.6 mmol) sodium hydride in 0.5 ml dimethylsulfoxide under argon atmosphere 132 mg (0.6 mmol) trimethyloxosulfonium iodide and 88 mg (0.5 mmol) **12** were added. After stirring for 90 min at room temperature, the reaction mixture was quenched with water. MTBE was added, the phases were separated and the aqueous phase was extracted with MTBE. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (MTBE:PE = 1:10) to give a colourless oil (33%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.85 (2H, m), 5.02 (4H, m), 2.41 (1H, dd, J = 16 Hz, 7 Hz), 2.24 (3H, m), 1.92-1.74 (2H, m), 1.46 (1H, m), 1.12 (1H, d, J = 5 Hz),0.88 (1H, d, J = 5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz): δ = 215.2 (C), 138.1 (CH), 135.7 (CH), 115.7 (CH_2), 114.9 (CH_2), 40.8 (C), 37.6 (C), 32.9 (CH_2), 32.4 (CH_2), 31.2 (CH_2), 30.4 (CH_2), 26.6 (CH_2), 24.7 (CH_2) ppm. IR ($CHCl_3$): ν = 3016, 1713, 1640, 917 cm^{-1}. MS: m/z (%) = 190 (12, M^+), 175 (16), 147 (59), 133 (86), 108 (87), 91 (78), 79 (100). HRMS calcd. for $C_{13}H_{18}O$ (M^+) 190.1358 found 190.1358.

General procedures for the synthesis of hydroazulenes

a) Typical procedure with methyltrioxorhenium.

3,3a,4,5,8,8a-Hexahydro-2H-azulen-1-one (17).

7 mg (0.028 mmol) Methyltrioxorhenium in 0.5 ml CH_2Cl_2 were added to a suspension of 0.5 g finely ground Strem carrier (87% SiO_2; 13% Al_2O_3; Strem Chemicals Inc.) in 4 ml 1,1,2-trichlorotrifluoroethane (TTE) under an argon atmosphere (glove box). After stirring for 10 min at room temperature a solution of 58 mg (0.33 mmol) 2-allyl-3-but-3-enyl-cyclopentanone **(13)** in 3 ml TTE was added. The reaction mixture was refluxed for 5 days and the progress of the reaction was monitored by GC/MS. The catalyst was then filtered off and the solvent evaporated under reduced pressure.

The crude product was purified by flash column chromatography (Et_2O:pentane = 1:20) to give a colourless oil (80%). The stereochemistry was assigned by NOE. ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.80 (2H, m), 2.83 (1H, dd, J = 16 Hz, 7 Hz), 2.06 (1H, m), 2.00 (1H, dd, J = 19 Hz, 8.5 Hz), 1.76 (3H, m), 1.51 (1H, m); 1.35 (2H, m), 1.18 (1H, m), 0.95 (2H, m) ppm. ^{13}C NMR (C_6D_6, 100.64 MHz): δ = 215.9 (C), 132.3 (CH), 130.2 (CH), 54.6 (CH), 48.2 (CH), 36.3(CH_2), 33.2 (CH_2), 28.1 (CH_2), 27.7 (CH_2) ppm; 2 C-atoms have the same shift. IR ($CHCl_3$): ν = 3018, 2928, 1735, 1204 cm^{-1}. MS: m/z (%) = 150 (98, M^+), 135 (22), 106 (27), 96 (36), 79 (64), 57 (100). HRMS calcd. for $C_{10}H_{14}O$ (M^+) 150.1045 found 150.1045.

8a-Methyl-3,3a,4,5,8,8a-hexahydro-2H-azulen-1-one (18).

Procedure a; solvent: TTE; 7 mg (0.028 mmol) MTO; 1 g Strem carrier; 58 mg (0.33 mmol) 2-allyl-3-but-3-enyl-2-methyl-cyclopentanone **(8)**; reaction time: 7 days.

The crude product was purified by flash column chromatography (Et_2O:pentane = 1:40 $\rightarrow$ 1:20) to give 31 mg (0.19 mmol, 58%) of a colourless oil. The stereochemistry was assigned by NOE. ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.76 (1H, m), 5.67 (1H, m), 2.67 (1H, dd, J = 15.5 Hz, 8.5 Hz), 2.09 (1H, dd, J = 19 Hz, 9 Hz), 2.04 (1H, m), 1.94-1.71 (3H, m), 1.38 (2H, m), 1.22 (2H, m), 1.13 (1H, m), 0.72 (3H, s) ppm. ^{13}C NMR (C_6D_6, 100.64 MHz): δ = 219.1 (C), 131.6 (CH), 128.0 (CH), 51.0 (CH), 48.4 (C), 35.5 (CH_2), 35.1 (CH_2), 29.0 (CH_2), 26.2 (CH_2), 25.5 (CH_2), 13.9 (CH_3) ppm. IR ($CHCl_3$): ν = 3025, 1731, 1205 cm^{-1}. MS: m/z (%) = 164 (63, M^+), 149 (76), 106 (100), 93 (66), 79 (47), 67 (31). HRMS calcd. for $C_{11}H_{16}O$ (M^+) 164.1201 found 164.1201.

3a-Methyl-3,3a,4,5,8,8a-hexahydro-2H-azulen-1-one (19a) + (19b).

Procedure a; solvent: TTE; 7mg (0.028 mmol) MTO; 0.5 g Strem carrier; 29 mg (0.15 mmol) 2-allyl-3-but-3-enyl-3-methyl-cyclopentanone **(14a)** + **(14b)** (in a ratio of 1.5:1.0); reaction time: 2 days.

The crude product was purified by flash column chromatography (MTBE:PE = 1:100) to give 34 mg (0.11 mmol; 73%) **19** as a yellow-brownish oil consisting of two diastereomers **19a** + **19b** in the ratio of 1.5 : 1.0 as assigned by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.81-5.70 (2H, m), 2.54-0.95 (11H, m), 1.18 (40% 3H, s), 0.85 (60% 3H, s) ppm. IR (CCl_4): ν = 2957, 2930, 1743, 1216 cm^{-1}. MS: m/z (%) = 164 (93, M^+), 149 (78),

131 (38), 120 (50), 107 (42), 105 (32), 93 (88), 91 (71), 79 (100), 67 (88), 55 (63), 53 (59). HRMS calcd. for $C_{11}H_{16}O$ (M^+) 164.1201 found 164.1201.

b) Typical procedure with the ruthenium catalyst.

3,4,5,8-Tetrahydro-2H-azulen-1-one (20).

To a solution of 3 mg ($3.3\ 10^{-3}$ mmol) ruthenium catalyst in 4 ml benzene a solution of 43 mg (0.244 mmol) **12** in 1 ml benzene was added under an argon atmosphere (glove box). After stirring at room temperature for 6 h a second portion of 3 mg ($3.3\ 10^{-3}$ mmol) ruthenium catalyst was added. The progress of the reaction was monitored by GC/MS. After 16 h air was passed through the reaction mixture. Then the solvent was evaporated under reduced pressure.

The crude product was purified by flash column chromatography (MTBE:PE = 1:4) to give 34 mg (0.23 mmol; 94%) **20** as a yellow-brownish oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.90 (1H, dt, J = 11 Hz, 5.5 Hz), 5.81 (1H, dt, J = 11 Hz, 5.5 Hz), 2.98 (2H, d, J = 5.5 Hz), 2.53-2.43 (4H, m), 2.39 (2H, t, J = 5.5 Hz), 2.34 (2H, t, J = 4.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 209.0 (C), 174.5 (C), 137.2 (C), 130.9 (CH), 129.0 (CH), 33.5 (CH_2), 31.4 (CH_2), 31.0 (CH_2), 24.6 (CH_2), 22.4 (CH_2) ppm. IR (CCl_4): ν = 2927, 1705 cm^{-1}. MS: m/z (%) = 149 (16, M^++1), 148 (100, M^+), 147 (22), 133 (36), 120 (18), 106 (33), 105 (49), 92 (28), 91 (90), 79 (28), 78 (33), 77(26), 57 (31), 55 (39). HRMS calcd. for $C_{10}H_{12}O$ (M^+) 148.0888 found 148.0888.

Tricyclo[5.3.1.0 1,7]undec-4-en-8-one (21).

Procedure b, solvent: 4.5 ml benzene; 2.6 mg ($2.83\ 10^{-3}$ mmol) ruthenium catalyst; 27 mg (0.141 mmol) **16**; after 20 h the reaction was completed.

The crude product was purified by flash column chromatography (MTBE:PE = 1:9) to give 23 mg (0.141 mmol; 100%) **21** as a yellow-brownish oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5,50 (1H, m), 5.40 (1H, m), 2.90 (1H, dd, J = 17.5 Hz, 6.5 Hz), 2.47-2.34 (1H, m), 2.22-2.09 (5H, m), 2.07-1.97 (1H, m), 1.94-1.82 (2H, m), 1.24 (1H, d, J = 5 Hz), 1.17 (1H, d, J = 5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 67.93 MHz): δ = 215.0 (C), 129.5 (CH), 126.2 (CH), 42.5 (C), 35.7 (C), 33.4 (CH_2), 30.5 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 25.5 (CH_2), 25.2 (CH_2) ppm. IR (CCl_4): ν = 2929, 1726 cm^{-1}. MS: m/z (%) = 163 (2, M^++1), 162 (12, M^+), 161 (3), 147 (8), 134 (32), 133 (100), 120 (9), 119 (10), 109 (15), 108 (16), 105 (37), 91 (33), 79 (34), 56 (20), 55 (21). HRMS calcd. for $C_{11}H_{14}O$ (M^+) 162.1045 found 162.1045.

11-Oxa-tricyclo[5.3.1.0 1,7]undec-4-en-8-one (22).

Procedure b; solvent: 5 ml benzene; 2.9 mg ($3.12\ 10^{-3}$ mmol) ruthenium catalyst; 32 mg (0.166 mmol) **15**; after 7 h a second portion of 2.9mg ($3.12\ 10^{-3}$ mmol) ruthenium catalyst was added. After 24 h the reaction was completed.

The crude product was purified by flash column chromatography (MTBE:PE = 1:9) to give 27 mg (0.164 mmol; 99%) **22** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.72 (1H, m), 5.50 (1H, m), 2.96 (1H, dd, J = 18 Hz,

6.5 Hz), 2.59 (1H, dm, J = 18 Hz), 2.39 (1H, ddd, J = 18 Hz, 9.5 Hz, 8.5 Hz), 2.32-2.16 (3H, m), 2.13-1.99 (3H, m), 1.90 (1H, ddd, J = 14 Hz, 9 Hz, 8.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 67.93 MHz): δ = 211.5 (C), 131.1 (CH), 124.7 (CH), 71.6 (C), 65.6 (C), 31.5 (CH_2), 29.3 (CH_2), 27.0 (CH_2), 22.3 (CH_2), 21.7 (CH_2) ppm. IR (CCl_4): ν = 2933, 1747) cm^{-1}. MS: m/z (%) = 165 (8, M^++1), 164 (68, M^+), 149 (8), 148 (7), 136 (48), 135 (39), 121 (28), 107 (40), 94 (45), 93 (44), 91 (37), 79 (100), 68 (77). HRMS calcd. for $C_{10}H_{12}O_2$ (M^+) 164.0837 found 164.0837.

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