# Ready Access to Bicyclo[5.3.0]decan-1-ones and to Bicyclo[6.3.0]undecan-1-ones by Intramolecular Pauson−Khand Reactions Using a Temporary Sulfur Bridge

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An intramolecular Pauson−Khand-based route to octahydroazulenones and decahydrocyclopentacyclooctenones is described. The amine oxide-induced cycloaddition of the dicobalt hexacarbonyl complexes of the sulfur-bridged enynes **1** and **2** leads to the exclusive formation of the tricyclic cyclopentenones **3** and **4**, respectively. This stereochemical outcome, which implies that the olefin moieties in both **1** and **2** react by the less substituted α-face, is rationalized on the basis of the steric requirements of the putative cobaltacyclic intermediates of the Pauson−Khand reaction. The totally stereoselective conjugate addition of methyl or phenyl groups to enones **3** and **4**, effected by the corresponding lithium diorganocuprates, and the subsequent reductive desulfurization with Raney nickel in refluxing ethanol, lead to the *cis*-bicyclo[5.3.0]decan-2-ones **5a**,**b** and to the *cis*-bicyclo[6.3.0]undecan-2-one **6**, respectively, in good overall yields. The stereochemistry of intermediates **3**, **4**, **7b**, **8**, and **9** has been firmly established with the aid of both NOESY experiments and AM1 semiempirical MO calculations.

## Introduction

Natural products with perhydroazulene (bicyclo[5.3.0]-decane) or perhydrocyclopentacyclooctene (bicyclo[6.3.0]-undecane) skeletons have been in recent years the object of much attention from the synthetic point of view.[1] Both the level of molecular complexity and the wide range of biological activities displayed by these natural products have provided the impetus for developing efficient methodologies aimed at the construction of cyclopentanoid rings fused to seven- or to eight-membered carbocycles.[2] However, due to the conformational flexibility of the perhydroazulene and perhydrocyclopentacyclooctene ring systems, the stereocontrolled elaboration of stereogenic centers embedded in these bicyclic systems still remains a challenging synthetic task.

Some of the most successful strategies that have been devised for the construction of these molecular systems are based on transition metal-mediated cyclization processes.[3−8] However, the Pauson−Khand reaction,[9] which stands out as a very powerful method for the one-step construction of cyclopentenones with high stereo- and regioselectivity, and which has been widely employed in the synthesis of natural products, either in racemic[10] or in enantiomerically pure form,[11] has been up to now largely unsuccessful in the preparation of perhydroazulene or perhydrocyclopentacyclooctene systems. Thus, the intermolecular version of the reaction is practically

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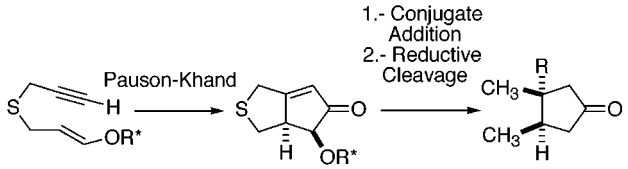
**Scheme 1**



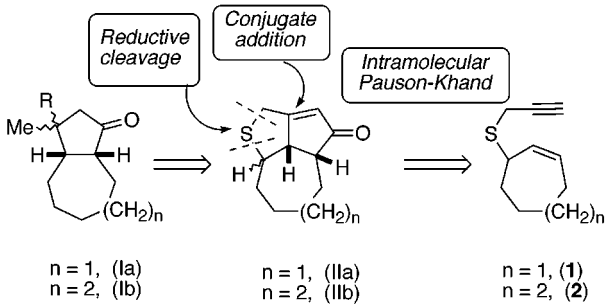

restricted to the use of strained, reactive olefins and, in fact, both cycloheptene and cyclooctene react only at high temperatures with the dicobalt hexacarbonyl complexes of terminal alkynes, affording the corresponding bicyclic enones in low yields.[12,13] On the other hand, the intramolecular version of the Pauson−Khand reaction has seldom been used for the construction of bicyclic systems other than bicyclo[3.3.0]oct-1-en-3-ones and bicyclo[4.3.0]non-1(9)-en-8-ones. Only recently, Cazes et al.[14] have reported the first construction of bicyclo[5.3.0]deca-1,7-dien-9-ones (albeit in rather low yields) by the *N*-oxide promoted Pauson−Khand bicyclization of nona-1,2-dien-8-ynes, while Schreiber and co-workers had previously employed the reaction for building an oxabicyclo[3.3.0]octenone system on a preformed eight-membered ring as one of the key steps in the total synthesis of (+)-epoxydictymene.[15]

We have recently reported the use of propargyl thiol as a synthon of propyne with reversed regioselectivity through the intramolecular Pauson−Khand reaction of allyl propargyl ethers followed by reductive cleavage (Scheme 1), and we have employed this strategy in an enantioselective synthesis of (+)-$\beta$-cuparenone.[11d,16] We wish now to report in detail an extension of this strategy which allows the efficient and stereoselective synthesis of both *cis*-bicyclo[5.3.0]decan-8-ones and *cis*-bicyclo[6.3.0]decan-9-ones, thus providing a direct entry to the guaiane and to the homoguaiane skeletons.

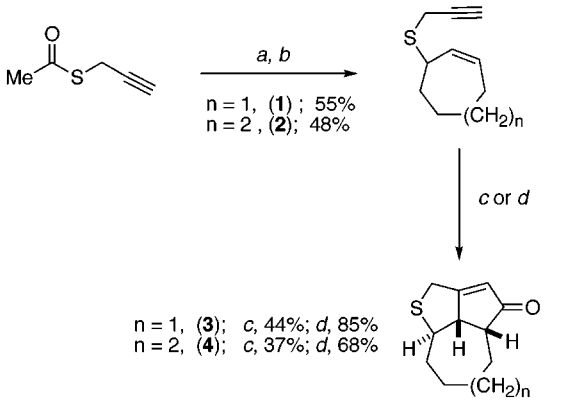
## Results and Discussion

As outlined in Scheme 2, we based our approach in the assumption that both the bicyclo[5.3.0]decan-8-one (Ia) and the bicyclo[6.3.0]decan-9-one systems (Ib) could be derived from the tricyclic enones IIa and IIb, respectively, by means of successive conjugate addition and reductive desulfurization protocols. IIa and IIb would in turn arise from the intramolecular Pauson−Khand reaction of the

**Scheme 2**




**Scheme 3**[a]




[a] Reaction conditions (a) $LiAlH_4$ (1 equiv), $Et_2O$, -40 °C. (b) 2 equiv of 2-cycloheptenyl bromide (**1**) or 2-cyclooctenyl bromide (**2**), HMPA, 50 °C, 4 h. (c) $Co_2(CO)_8$ (1.1 equiv), isooctane, rt, 2 h; reflux, 0.5 h. (d) $Co_2(CO)_8$ (1.2 equiv), $CH_2Cl_2$, rt, 2 h; NMO (6 equiv), rt, 12 h.

enynes **1** (leading to IIa) and **2** (for IIb). A cis configuration for the ring fusion in both Ia and Ib would be clearly expected on the basis of the known high selectivity of the Pauson−Khand cycloaddition, but the relative configuration of C-3 (in Ia or Ib), determined by the stereofacial selectivity of the conjugate addition in the tricyclic intermediates IIa,b, was not easily predictable at the outset of our experiments.

The requisite enyne **1** was easily assembled by the reaction of 2-cycloheptenyl bromide (prepared by the treatment of cycloheptene by NBS in $CCl_4$)[17] with lithium 2-propynethiolate (generated by the in situ reduction of propargyl thioacetate with lithium aluminum hydride in ethyl ether)[18] at 50 °C during 5 h in the presence of HMPA; after chromatographic purification, **1** was obtained in 55% yield (Scheme 3). The addition of **1** to an isooctane solution of $Co_2(CO)_8$ led to the formation of the corresponding dicobalt hexacarbonyl complex (room temperature, 1 h), which was thermally decomposed (90 °C, 1 h) to afford the diastereomerically pure tricyclic enone **3** as a crystalline solid in 44% yield. This yield was substantially improved (up to 85%) by promoting the reaction with *N*-methylmorpholine *N*-oxide,[19] which again produced **3** as a single diastereomer (by $^{13}C$ NMR). The 8−5−5 tricyclic Pauson−Khand adduct **4** was prepared in a similar way: enyne **2** was obtained by reacting

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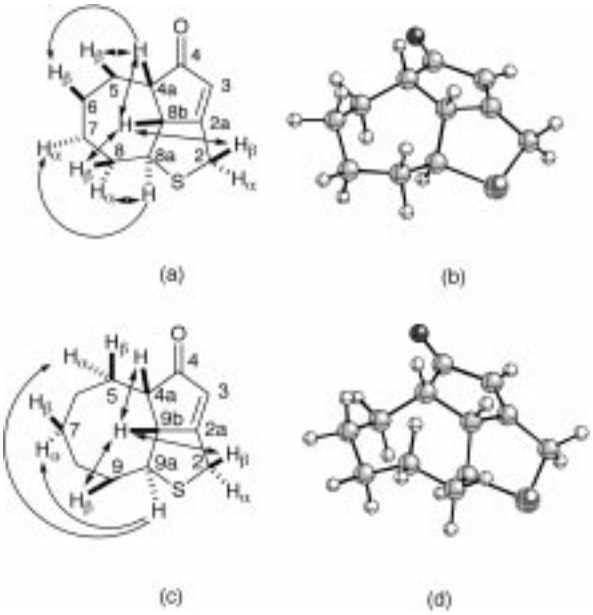



**Figure 1.** Selected NOESY correlations and AM1-calculated lowest-energy conformations of compounds **3** (a, b) and **4** (c, d).

2-cyclooctenyl bromide with lithium 2-propynethiolate, and its dicobalt hexacarbonyl complex was cyclized under thermal and *N*-oxide-mediated conditions to give diastereomerically pure **4** in 37% and 68% yield, respectively.

At this point, we addressed the crucial issue of the relative configuration of the three contiguous stereogenic centers in compounds **3** and **4**. According to the well-established stereospecificity of the Pauson−Khand reaction, the cis-nature of the ring fusion of the cyclopentenone with the seven- or eight-membered ring is fixed as a consequence of the cis stereochemistry of the cycloalkene. However, the relative configuration of the remaining stereogenic center (8a for **3** and 9a for **4**; see Figure 1 for numbering) had to be rigurously established, since the Pauson−Khand cycloaddition could have taken place on any of the two diastereotopic faces of the olefins in enynes **1** and **2**. To do this, we carried out extensive 1D and 2D NMR studies, which allowed us to assign all of the $^{1}$H and $^{13}$C signals for the tricyclic enone **3** (see Supporting Information); at this point, standard NOESY experiments unambiguously established the relative configuration of stereocenters 4a, 8b and 8a (Figure 1a). In effect, a NOESY cross-peak between the resonances of H8b and H4a confirmed the cis-union of the cycloheptene and the cyclopentenone rings, but H8a did not show any NOE correlation neither with H8b nor with H4a; moreover, the NOESY spectrum of **3** univocally related the *β*-face hydrogens (H2*β*, H4a, H5*β*, H6*β*, H8b, and H8*β*), on one side, and the α-face hydrogens (H5α, H7α, H8a, and H8α) on the other. These assignments were fully confirmed by inspection of the geometry of the more stable conformer of **3**, calculated at the AM1 level of theory[20] (see Figure 1b). It is worth noting that these theoretical studies also indicate that **3** is ca. 1.7 kcal mol$^{-1}$ more stable than the corresponding epimer at C8a. The relative configuration of the stereogenic centers of **4** could also be determined by NMR (see Figure 1c). Although

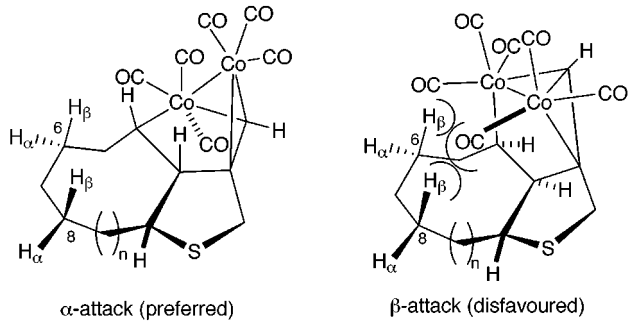



**Figure 2.** Schematic representation of the two possible intermediate cobaltacycles in the Pauson−Khand cyclization of enynes **1** and **2**.

in this case the higher complexity of the $^{1}$H spectrum did not allow us to assign unambiguously all of the signals, the two cis ring-junction protons H9b and H4a showed a clear NOE correlation, but none of them exhibited an NOE interaction with the topologically contiguous H9a; on the other hand, this proton presented NOE cross-peaks both with H5α and H7α. Again, these observations are in full agreement with the geometry of the AM1-calculated lowest energy conformer of **4** (Figure 1d), which is 5.2 kcal mol$^{-1}$ more stable than the less energetic conformation of the epimer at 9a.

This stereochemical outcome can be easily rationalized in the framework of the currently accepted mechanistic model of the Pauson−Khand reaction,[21] if one assumes that the intermediate cobaltacycles adopt conformations similar to those depicted for **3** and **4** in Figures 1b and 1d, respectively; as shown in Figure 2, while the cobaltacycle arising from the attack of the complex at the *β*-face of the olefin would be strongly destabilized by the steric repulsion of the CO ligands of one cobalt with H6*β* and H8*β*, the cobaltacycle obtained through attack at the α-face is free of these repulsive interactions and leads to the observed adducts **3** and **4** (see Figure 2). This hypothesis has been fully supported by semiempirical MO calculations at the PM3-(tm) level,[20] which show that the cobaltacycles resulting from cobalt coordination at the α-face of the olefin are much more stable than those resulting from *β*-face coordination (see Figure 3 for the optimized structures and energies).

The conversion of the Pauson−Khand adducts into the bicyclic ketones **5a**,**b** and **6** is summarized in Scheme 4. We shall first discuss the preparation of the octahydroazulenones **5a**,**b**. The conjugate addition of both methyl and phenyl was achieved by reaction with lithium dimethyl cuprate and lithium diphenyl cuprate (generated by the treatment of the corresponding organolithium compound with cuprous iodide and with cuprous cyanide, respectively), and took place exclusively on the *β*-face of enone **3**, affording the tricyclic ketones **7a** and **7b** in 76% and 74% yield, respectively. The catalytic hydrogenation (10% Pd/C, ethanol) was also totally stereoselective and gave the ketone **8** as a single diastereomer. These stereochemical assignments are in complete accordance with the outcome of NOESY experiments performed on compounds **7b** and **8** (see Figure 4). Finally, the Raney nickel-induced desulfurization of **7a** and **7b** led to the

(20) The calculations were performed with the semiempirical MO AM1 or PM3-tm programs, as implemented in MacSpartan *Plus* (Wavefunction, Inc.).

(21) (a) Magnus, P. C.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861−5869. (b) Magnus, P. C.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851−4854. (c) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 6541−6556.

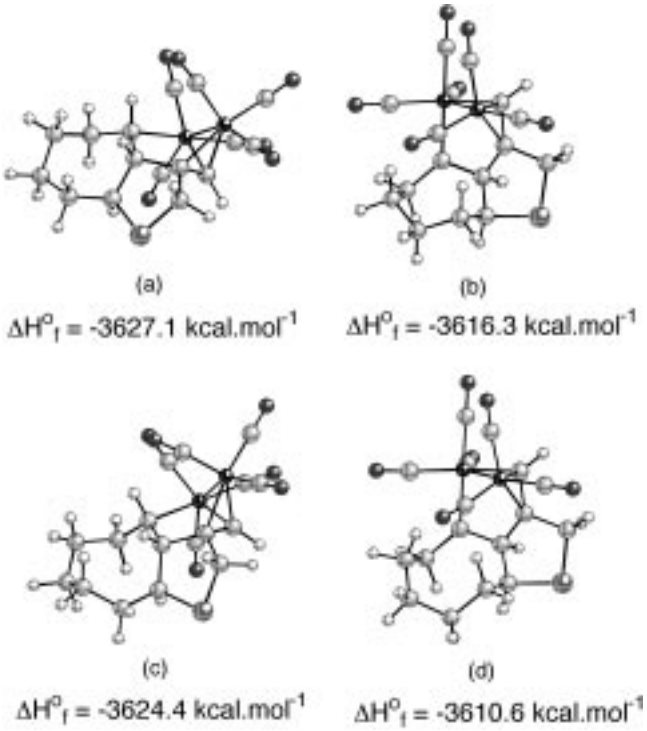
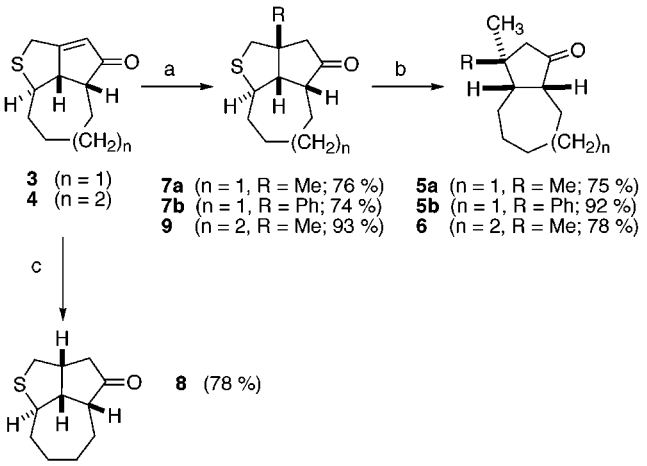



**Figure 3.** PM3-tm calculated structures and energies of the cobaltacyclic intermediates of the Pauson−Khand reaction of enynes **1** (a, α-attack; b, *β*-attack) and **2** (c, α-attack; d, *β*-attack).

**Scheme 4**[a]




[a] Reaction conditions: (a) MeLi (3 equiv), CuI (1.5 equiv) (R = Me) or PhLi (3 equiv), CuCN (1.5 equiv) (R = Ph), $Et_2O$, −10 to 0 °C, 10 min; **3** or **4**, rt, 12 h. (b) Raney nickel, EtOH, reflux, 2 h. (c) 10% Pd−C, $H_2$ (1 atm), EtOH, rt, 24 h.

corresponding crude hydroazulenones **5a** and **5b** in good yields. It is important to note here that, upon attempted purification by column chromatography on silica gel, **5b** underwent partial epimerization at C1; in fact, the treatment of **5b** with potassium carbonate in methanol[22] led to a 12:88 mixture of **5b** and its trans diastereomer **10** (estimated by NMR). These observations were supported by the result of AM1 calculations,[20] which established that **10** is somewhat more stable than **5b**. On the other hand, the preparation of the bicyclic undecanone

(22) For a related example, see: Paquette, L. A.; Romine, J. L.; Lin, H.-S.; Wright, J. *J. Am. Chem. Soc.* **1990**, *112*, 9284−9292.

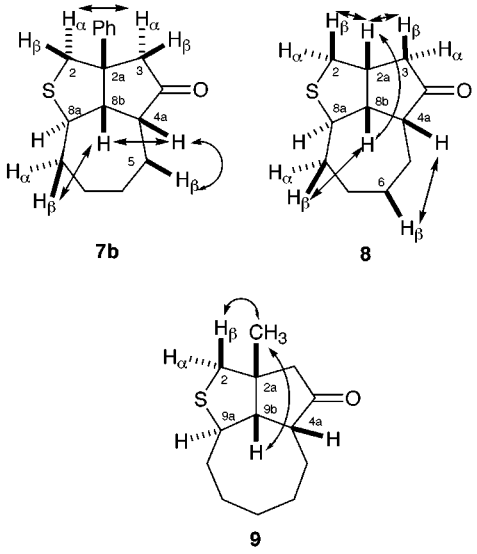
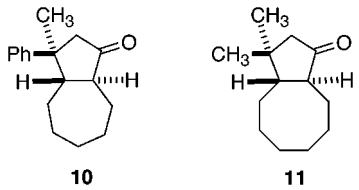



**Figure 4.** Selected NOESY correlations for compounds **7b**, **8**, and **9**.

**6** was totally parallel to that of **5a**: lithium dimethyl cuprate mediated conjugate addition gave the stereoisomerically pure tricyclic ketone **9** in excellent yield (93%), and the treatment of **9** with Raney nickel in boiling ethyl alcohol, followed by filtration through Celite, afforded *cis*-3,3-dimethyldecahydrocyclopentacycloocten-1-one (**6**) in 78% yield. As observed for **5b**, the exposure of **6** to potassium carbonate in methanol resulted in the formation of a 14:86 mixture (determined by GC) of **6** and its trans-isomer **11**, which is 2.2 kcal $mol^{-1}$ more stable than **6**, according to AM1 calculations. The stereochemistry of compound **9** was again firmly established by a NOESY experiment (see Figure 4).




In summary, we have shown that the intramolecular Pauson−Khand reaction of 3-(prop-2-ynylsulfanyl)cycloalkenes **1** and **2**, followed by conjugate addition and reductive cleavage of a tetrahydrothiophene ring, constitutes a new, efficient, and totally diastereoselective route to *cis*-perhydroazulenes and *cis*-perhydrocyclopentacyclooctenes, which can be of interest for the synthesis of natural products with these bicyclic skeletons.

## Experimental Section

**General.** Melting points were determined in an open capillary tube and are uncorrected. Infrared spectra were recorded in Fourier transform mode, using film (NaCl) or KBr pellet techniques. $^1H$ NMR spectra were recorded at 200, 300, or 500 MHz in $CDCl_3$ unless specified otherwise. $^{13}C$ NMR spectra were recorded at 50.3, 62.9, or 75.4 MHz in $CDCl_3$ unless specified otherwise, with $CHCl_3$ as internal standard. Signal multiplicities were established by DEPT experiments. Mass spectra were recorded at 70 eV ionizing voltage; ammonia was used for chemical ionization (CI). Elemental analyses were performed by the "Servei d'Anàlisis Elementals del CSIC de Barcelona". THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was

distilled from $CaH_2$. Hexamethyl phosphoramide (HMPA) was purified by distillation at reduced pressure, and stored over 4 Å molecular sieves. All reactions were performed in flame or oven-dried glassware under a $N_2$ or Ar atmosphere. Reaction progress was followed by TLC. Silica gel (70−230 mesh) was used for column chromatography. 3-Bromocycloheptene and 3-bromocyclooctene were obtained by allylic halogenation of the corresponding cycloalkenes with *N*-bromosuccinimide and benzoyl peroxide according to a described procedure.[17]

**3-(Prop-2-ynylsulfanyl)cycloheptene, 1.** To a cold (−40 °C), stirred suspension of lithium aluminum hydride (0.30 g, 8.0 mmol) in dry diethyl ether (4 mL), under nitrogen, was carefully added dropwise a solution of propargyl thioacetate (1.00 g, 8.8 mmol) in diethyl ether (2 mL); the resulting solution was allowed to attain room temperature and stirred for 1 h. After cooling again to −40 °C, 3-bromocycloheptene (2.79 g, 15.9 mmol) in HMPA (1 mL) was added via syringe, and the reaction flask was warmed to 50 °C during 4 h. The excess hydride was eliminated by sequential treatment with water (0.3 mL), aqueous 15% NaOH solution (0.3 mL), and water (0.6 mL). The clear supernatant was separated by decantation and dried over $MgSO_4$. The solvent was distilled at reduced pressure, and the crude product was purified by column chromatography, eluting with hexane−diethyl ether mixtures of increasing polarity, to give 0.83 g (55% yield) of the cycloheptenyl propargyl sulfide **1**. Colorless oil. IR (film) $\nu_{max}$ 3300, 2120, 790, 630 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 6.0−5.6 (m, 2H), 3.90−3.75 (m, 1H), 3.25 (dd, $J = 2.6$ Hz, $J' = 0.8$ Hz, 2H), 2.24 (t, $J = 2.6$ Hz, 1H), 2.3−1.4 (m, 8H). $^{13}C$ NMR (50.3 MHz): $\delta$ 133.9 (CH), 131.8 (CH), 80.1 ($C_q$), 70.7 (CH), 44.9 (CH), 31.7 ($CH_2$), 28.2 ($CH_2$), 27.0 ($CH_2$), 26.9 ($CH_2$), 18.5 ($CH_2$). MS (EI): $m/z = 166$ ($M^+$, 2%), 95 ($[M - SC_3H_3]^+$, 100%).

**3-(Prop-2-ynylsulfanyl)cyclooctene, 2.** Prepared by the procedure described above for **1**, in 48% yield. Colorless oil. IR (film): $\nu_{max}$ 3300, 2120, 770, 630 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 5.6−5.9 (m, 2H), 5.35−5.50 (m, 1H), 3.95−4.15 (m, 1 H), 3.4−3.1 (m, 2H), 2.24 (t, $J = 2.6$ Hz, 1H), 2.3−2.0 (m, 2H), 2.0−1.1 (m, 8H). $^{13}C$ NMR (50.3 MHz): $\delta$ 132.5 (CH), 132.3 (CH), 80.6 ($C_q$), 70.6 (CH), 40.8 (CH), 34.8 ($CH_2$), 29.5 ($CH_2$), 26.8 ($CH_2$), 26.6 ($CH_2$), 25.9 ($CH_2$), 18.5 ($CH_2$). MS (CI): $m/z = 198$ ($[M + 18]^+$, 15%), 215 ($[M + 35]^+$, 100%).

**(4a*RS*,8a*RS*,8b*RS*)-(2,4a,5,6,7,8,8a,8b)-Octahydro-1-thiacyclopenta[*cd*]azulen-4-one, 3.** (a) Thermal Reaction. To a stirred solution of $Co_2(CO)_8$ (0.41 g, 1.2 mmol) in isooctane (40 mL), under argon, was added dropwise a solution of the enyne **1** (0.18 g, 1.1 mmol) in isooctane (40 mL); the resulting solution was stirred at room temperature until complete disappearance of the starting material (TLC) and was subsequently heated for 4 h at 90 °C. The reaction mixture was cooled to room temperature and filtered through Celite, which was thoroughly washed with dichloromethane. The solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography, eluting with hexane−methylene chloride mixtures of increasing polarity, to give 0.12 g (44% yield) of the tricyclic ketone **3**. (b) *N*-Oxide-Promoted Reaction. To a stirred solution of $Co_2(CO)_8$ (90 mg, 0.26 mmol) in dry dichloromethane (8 mL) under Ar at room temperature was added dropwise a solution of the enyne **1** (40 mg, 0.24 mmol) in dichloromethane (2 mL). After 2 h of stirring at room temperature, solid *N*-methylmorpholine *N*-oxide (0.17 g, 1.4 mmol) was added in one portion. Although the reaction was complete after 1/2 h, as shown by TLC, the reaction mixture was left overnight in order to settle the violet coprecipitate out. After filtration through Celite, which was thoroughly washed with methylene chloride, the solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography (eluting with hexane-methylene chloride mixtures of increasing polarity) to give 40 mg (85% yield) of **3**. Colorless solid. Mp: 72.0−72.5 °C. IR (KBr): $\nu_{max}$ 1694, 1626 $cm^{-1}$. $^1H$ NMR (500 MHz): $\delta$ 5.91 (s, 1H), 3.87 (part A of AB system, $J = 15.5$ Hz, 1H), 3.76 (part B of AB system, $J = 15.5$ Hz, 1H-), 3.20−3.13 (m, 1H), 3.01 (td, $J = 11.5$, $J' = 2$ Hz, 1H), 2.62 (pseudo-quint, $J = 6.5$ Hz, 1H), 2.18 (pseudo-quint, $J = 5.5$ Hz, 1H), 2.10−2.00 (m, 2H), 1.98−1.90 (m, 1H), 1.55−1.42 (m, 1H), 1.40−1.20 (m, 2H), 1.20−1.08 (m, 1H). $^{13}C$ NMR (75.4 MHz): $\delta$ 210.8 ($C_q$), 181,5 ($C_q$), 125.9 (CH), 59.5 (CH), 49.8 (CH), 47.9 (CH), 33.2 ($CH_2$), 31.4 ($CH_2$), 30.5 ($CH_2$), 27.5 ($CH_2$), 26.7 ($CH_2$). MS (CI): $m/z = 195$ ($[M + 1]^+$, 2%), 212 ($[M + 18]^+$, 76%), 229 ($[M + 35]^+$, 100%).

**(4a*RS*,9a*RS*,9b*RS*)−(4a,5,6,7,8,9,9a,9b)-Octahydro-2*H*-1-thiacycloocta[*cd*]pentalen-4-one, 4.** Obtained in 37% yield by the procedure (a) described above for **3**, and in 68% yield by the procedure (b) described above for **3**. Colorless solid. Mp: 61.0−62.5 °C. IR (KBr): $\nu_{max}$ 1700, 1630 $cm^{-1}$. $^1H$ NMR (500 MHz): $\delta = 5.95$ (s, 1H), 3.77 (part A of AB system, $J = 15$ Hz, 1H), 3.68 (part B of AB system, $J = 15$ Hz, 1H), 3.26 (td, $J = 11$ Hz, $J' = 3$ Hz, 1H), 3.11−3.04 (m, 1H), 2.37 (dd, $J = 11.5$, $J' = 7$ Hz, 1H), 2.04−1.96 (m, 2H), 2.8−2.2 (m, 7H). $^{13}C$ NMR (75.4 MHz): $\delta$ 211.9 ($C_q$), 183.2 ($C_q$), 125.0 (CH), 55.9 (CH), 50.3 (CH), 46.0 (CH), 36.6 ($CH_2$), 30.2 ($CH_2$), 30.1 ($CH_2$), 25.6 ($CH_2$), 25.4 ($CH_2$), 25.1 ($CH_2$).). MS (CI): $m/z = 209$ ($[M + 1]^+$, 5%), 226 ($[M + 18]^+$, 100%), 243 ($[M + 35]^+$, 74%).

**(2a*SR*,4a*RS*,8a*RS*,8b*RS*)-2a-Methyl-octahydro-1-thia-cyclopenta [*cd*]azulen-4-one, 7a.** To a cold (−10 °C) suspension of prepurified CuI (75 mg, 0.40 mmol) in anhydrous diethyl ether (1 mL) was added dropwise a 1.6 M solution of methyllithium in diethyl ether (0.5 mL, 0.79 mmol). After stirring for 10 min at 0 °C, the resulting light green suspension was cooled at −50 °C and treated with a solution of **3** (50 mg, 0.26 mmol) in diethyl ether/THF (1/1, 2 mL). The reaction mixture was slowly allowed to warm to room temperature, stirred overnight, and poured into a mixture of diethyl ether (20 mL), aqueous saturated $NH_4Cl$ (30 mL), and crushed ice. The phases were separated, and the organic layer was washed with aqueous saturated $NH_4Cl$ until no more blue color developed in the aqueous layer. The aqueous phases were extracted with diethyl ether (20 mL) and methylene chloride (20 mL), and the combined organic extracts were washed with brine. Drying over $Na_2SO_4$ and elimination of the solvents at reduced pressure gave a crude product which was purified by column chromatography, eluting with hexane/methylene chloride (20/1), to afford 42 mg (76%) of the tricyclic ketone **7a**. Colorless solid. Mp: 68.5-69.2 °C. IR (KBr): $\nu_{max}$ 1740 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 3.24 (td, $J = 10.6$, $J' = 2$ Hz, 1H), 3.04 (part A of AB system, $J = 11$ Hz, 1H), 2.92 (part B of AB system, $J = 11$ Hz, 1H), 2.84−2.66 (m, 1H), 2.44 (part A of AB system, $J = 18$ Hz, 1H), 2.16 (part B of AB system, $J = 18$ Hz, 1H), 2.40−2.04 (m, 3H), 2.0−1.7 (m, 2H), 1.6−1.2 (m, 4H), 1.26 (s, 3H). $^{13}C$ NMR (75.4): $\delta$ 219.3 ($C_q$), 62.4 (CH), 50.7 (CH), 50.7 (CH), 49.1 ($CH_2$), 42.7 ($CH_2$), 36.8 ($CH_2$), 30.8 ($CH_2$), 27.8 ($CH_2$), 27.0 ($CH_3$), 25.5 ($CH_2$). MS (CI): $m/z = 211$ ($[M + 1]^+$, 2%), 228 ($[M + 18]^+$, 85%), 245 ($[M + 35]^+$, 100%). Anal. Calcd for $C_{12}H_{18}OS$: C 68.57%, H 8.57%, S 15.24%. Found: C 68.49%, H 8.79%, S 15.19%.

**(2a*RS*,4a*RS*,8a*RS*,8b*RS*)-2a-Phenyl-octahydro-1-thia-cyclopenta[*cd*]azulen-4-one, 7b.** The procedure described above for **7a** was used, with the following reagents and quantities: CuCN (23 mg, 0.26 mmol); 1.6 M PhLi in cyclohexane/diethyl ether (0.32 mL, 0.53 mmol); enone **3** (34 mg, 0.17 mmol). After chromatographic purification, 25 mg (74% yield) of the tricyclic ketone **7b** was obtained. Colorless solid. Mp: 116.0−117.0 °C; IR (KBr): $\nu_{max}$ 1740 $cm^{-1}$. $^1H$ NMR (500 MHz): $\delta$ 7.4−7.3 (m, 3H), 7.3−7.2 (m, 1H), 3.42−3.36 (m, 1H), 3.39 (part A of AB system, $J = 11.5$ Hz, 1H), 3.18 (part B of AB system, $J = 11.5$ Hz, 1H), 3.03−2.96 (m, 1H), 3.00 (part A of AB system, $J = 17.5$ Hz, 1H), 2.73 (part B of AB system, $J = 17.5$ Hz, 1H), 2.50 (pseudo-q, $J = 9.5$ Hz, 1H), 2.23−2.10 (m, 2H), 1.97−1.90 (m, 1H), 1.85−1.75 (m, 1H), 1.68−1.58 (m, 1H), 1.42−1.23 (m, 3H). $^{13}C$ NMR (62.9 MHz): $\delta$ 218.0 ($C_q$), 144.4 ($C_q$), 128.9 ($CH_2$), 127.0 (CH), 125.6 ($CH_2$), 63.1 (CH), 58.2 ($C_q$), 50.5 (CH), 50.5 (1CH), 47.5 ($CH_2$), 44.3 ($CH_2$), 36.7 ($CH_2$), 30.81 ($CH_2$), 27.8 ($CH_2$), 25.4 ($CH_2$).). MS (CI): $m/z = 273$ ($[M + 1]^+$, 6%), 290 ($[M + 18]^+$, 100%), 307 ($[M + 35]^+$, 18%). Anal. Calcd for $C_{17}H_{20}OS$: C 75.00%, H 7.35%, S 11.76%. Found: C 74.89%, H 7.06%, S 11.63%.

**(2a*SR*,4a*RS*,9a*RS*,9b*RS*)-2a-Methyl-decahydro-1-thia-cycloocta[*cd*]pentalen-4-one, 9.** Obtained in 93% yield by the procedure described above for **7a**. Colorless solid. Mp:

91.0−92.0 °C; IR (KBr): $\nu_{max}$ 1736 cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 3.28−3.24 (m, 1H), 3.07 (part A of AM system, $J$ = 11.5 Hz, 1H), 2.76 (part M of AM system, $J$ = 11.5 Hz, 1H), 2.56 (part A of AM system, $J$ = 18.5 Hz, 1H), 2.44−2.35 (m, 2H), 2.12−2.02 (m, 2H), 2.07 (part M of AM system, $J$ = 18.5 Hz, 1H), 1.84−1.74 (m, 2H), 1.7−1.2 (m, 6H), 1.24 (s, 3H). $^{13}$C NMR (75.4 MHz): $\delta$ 219.1 ($C_q$), 59.8 (CH), 52.8 ($C_q$), 52.0 (CH), 49.5 (CH), 46.9 ($CH_2$), 41.6 ($CH_2$), 39.7 ($CH_2$), 27.0 ($CH_2$), 26.2 ($CH_3$), 24.9 ($CH_2$), 24.5 ($CH_2$), 23.6 ($CH_2$). MS (CI): $m/z$ = 225 ([M + 1]$^+$, 3%), 242 ([M + 18]$^+$, 100%), 259 ([M + 35]$^+$, 60%). Anal. Calcd for $C_{13}H_{20}OS$: C 69.64%, H 8.93%. Found: C 69.91%, H 9.29%.

**(2a*SR*,4a*RS*,8a*RS*,8b*RS*)-Octahydro-1-thiacyclopenta-[*cd*]azulen-4-one, 8.** A solution of enone **3** (0.14 g, 0.74 mmol) in ethanol (5 mL) was added to a suspension of 10% Pd−C (0.40 g) in ethanol (30 mL). The mixture was stirred at room temperature under hydrogen at 1 atm. After 2 h, an additional quantity of 10% Pd−C (0.30 g) was added and stirring was continued until TLC showed the complete disappearance of the starting compound (24 h). Filtration through a Celite pad and concentration led to 0.15 g of a solid which was purified by column chromatography, eluting with hexane/methylene chloride (7/3), to afford 113 mg (78% yield) of the ketone **8**. Colorless solid. Mp: 60.0−61.0 °C. IR (KBr): $\nu_{max}$ 1740 cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 3.33 (dd, $J$ = 11 Hz, $J'$ = 7 Hz, 1H), 3.18 (td, $J$ = 11, $J'$ = 2 Hz, 1H), 3.13−3.02 (m, 1H), 2.80−2.63 (m, 2H), 2.78 (dd, $J$ = 11 Hz, $J'$ = 1.5 Hz, 1H), 2.51 (ddt, $J$ = 19 Hz, $J'$ = 9 Hz, $J''$ = 1 Hz, 1H), 2.22−2.04 (m, 3H), 2.19 (dd, $J$ = 19 Hz, $J'$ = 11 Hz, 1H), 1.94−1.86 (m, 1H), 1.85−1.76 (m, 1H), 1.5−1.1 (m, 4H). $^{13}$C−RMN (75.4 MHz): $\delta$ 218.9 ($C_q$), 57.5 (CH), 52.3 (CH), 48.0 (CH), 44.5 (CH), 42.4 ($CH_2$), 36.2 ($CH_2$), 35.5 ($CH_2$), 30.9 ($CH_2$), 27.9 ($CH_2$), 25.5 ($CH_2$). MS (CI): $m/z$ = 197 ([M + 1]$^+$, 10%), 214 ([M + 18]$^+$, 100%), 231 ([M + 35]$^+$, 66%). Anal. Calcd for $C_{11}H_{16}OS$: C 67.35%, H 8.16%, S 16.32%. Found: C 67.27%, H 8.16%, S 16.30%.

***cis*-3,3-Dimethyl-octahydro-azulen-1-one, 5a.** A mixture of Raney nickel (3.0 g from a 50% aqueous suspension, rinsed with acetone and ethanol) and the ketone **7a** (36 mg, 0.17 mmol) in ethanol (3 mL) was heated to reflux until TLC analysis showed the complete disappearance of starting material (1 h). The Raney nickel was then filtered off and thoroughly rinsed with dichloromethane. Solvent evaporation at reduced pressure gave an oil which was filtered through Celite, eluting with hexane, to afford 23 mg (75% yield) of ketone **5a**. Colorless oil. IR (film): $\nu_{max}$ 1740 cm$^{-1}$. $^1$H NMR (300 MHz): $\delta$ 2.55−2.35 (m, 1H), 2.35−1.80 (m, 6H), 2.28 (part A of AB system, $J$ = 16.5 Hz, 1H), 2.09 (part B of AB system, $J$ = 16.5 Hz, 1H), 1.40−1.05 (m, 5H), 1.13 (s, 3H), 0.87 (s, 3H). $^{13}$C NMR (75.4 MHz): $\delta$ 220.1 ($C_q$), 55.0 ($CH_2$), 52.8 (CH), 51.1 (CH), 37.8 ($C_q$), 31.7 ($1CH_2$), 30.5 ($CH_2$), 28.1 ($CH_2$), 28.1 ($CH_3$), 27.7 ($CH_2$), 26.0 ($CH_2$), 23.8 ($CH_3$). MS (CI): $m/z$ = 198 ([M + 18]$^+$, 100%), 215 ([M + 35]$^+$, 74%).

**(3*RS*,3a*RS*,8a*SR*)-3-Methyl-3-Phenyl-octahydro-azulen-1-one, 5b.** Obtained in 92% yield by the procedure described above for **5a**. Colorless oil. IR (film): $\nu_{max}$ 1738 cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 7.5−7.1 (m, 5H), 2.93 (d, $J$ = 16.5 Hz, 1H), 2.80−2.74 (pseudo-dt, $J$ = 12 Hz, $J'$ = 4 Hz, 1H), 2.55−2.85 (m, 1H), 2.31 (d, $J$ = 16.5 Hz, 1H), 2.28−2.14 (m, 1H), 2.00−1.90 (m, 1H), 1.90−1.80 (m, 2H), 1.50−1.00 (m, 6H), 1.26 (s, 3H). $^{13}$C NMR (75.4 MHz): $\delta$ 218.9 ($C_q$), 146.7 ($C_q$), 128.3 (CH), 126.1 (CH), 125.8 (CH), 54.6 ($CH_2$), 52.2 (CH), 52.1 (CH), 44.8 ($C_q$), 31.6 ($1CH_2$), 30.2 ($CH_2$), 28.0 ($CH_2$), 27.8 ($CH_2$), 26.1 ($CH_2$), 22.1 ($CH_3$). MS (CI): $m/z$ = 243 ([M + 1]$^+$, 2%), 260 ([M + 18]$^+$, 100%), 277 ([M + 35]$^+$, 27%).

***cis*-3,3-Dimethyl-decahydro-cyclopentacycloocten-1-one, 6.** Obtained in 78% yield by the procedure described above for **5a**. Colorless oil. IR (film): $\nu_{max}$ 1740 cm$^{-1}$. $^1$H NMR (300 MHz): $\delta$ 2.30 (t, $J$ = 10.2 Hz, 1H), 2.21 (part A of AB system, $J$ = 16.5 Hz, 1H), 2.03 (part B of AB system, $J$ = 16.5 Hz, 1H), 2.15−1.10 (m, 13H), 1.14 (s, 3H), 0.76 (s, 3H). $^{13}$C NMR (75.4 MHz): $\delta$ 221.8 ($C_q$), 54.4 ($CH_2$), 52.4 (CH), 49.6 (CH), 39.1 ($C_q$), 31.9 ($CH_2$), 30.0 ($CH_2$), 27.4 ($CH_3$), 27.1 ($CH_2$), 26.1 ($CH_2$), 25.2 ($CH_2$), 22.4 ($CH_3$), 21.3 ($CH_2$). MS (CI): $m/z$ = 195 ([M + 1]$^+$, 2%), 212 ([M + 18]$^+$, 100%), 229 ([M + 35]$^+$, 12%).

**(3*RS*,3a*RS*,8a*RS*)-3-Methyl-3-Phenyl-octahydro-azulen-1-one, 10.** To a well-stirred suspension of potassium carbonate (2 mg) in methanol (0.5 mL) was added a solution of the ketone **5b** (10 mg, 0.04 mmol) in methanol (1 mL). The reaction mixture was stirred at 25 °C for 24 h. After removal of the solvent by rotary evaporation, the residue was dissolved in methylene chloride, filtered, washed with brine, and dried. The solvents were eliminated in vacuo, and the residue was purified by column chromatography, eluting with hexane−diethyl ether mixtures of increasing polarity, to afford 9 mg (90% yield) of a 12/88 (according to $^1$H NMR) mixture of **5b/10**. IR (film): $\nu_{max}$ 1738 cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 7.5−7.1 (m, 5H), 2.66 (dd, $J$ = 18 Hz, $J'$ = 1 Hz, 1H), 2.44 (dd, $J$ = 18 Hz, $J'$ = 1 Hz, 1H), 2.27−2.15 (m, 3H), 1.80−1.50 (m, 4H), 1.50−1.30 (m, 5H), 1.30 (s, 3H). $^{13}$C NMR (75.4 MHz): $\delta$ 219.8 ($C_q$), 146.7 ($C_q$), 128.3 (2CH), 126.1 (CH), 125.8 (2CH), 55.3 ($CH_2$), 52.5 (CH), 52.5 (CH), 43.8 ($C_q$), 28.5 ($CH_2$), 28.4 ($1CH_2$), 27.8 ($CH_2$), 26.8 ($CH_2$), 26.6 ($CH_2$), 20.5 ($CH_3$). MS (CI): $m/z$ = 243 ([M + 1]$^+$, 1%), 260 ([M + 18]$^+$, 100%), 277 ([M + 35]$^+$, 23%).

***trans*-3,3-Dimethyl-decahydro-cyclopentacycloocten-1-one, 11.** Obtained in 99% yield as a 14/86 mixture (determined by GC) of **6/11** by the procedure described above for **10**. $^1$H NMR (300 MHz): $\delta$ 2.09 (dd, $J$ = 8.1 Hz, $J'$ = 1.2 Hz, 2H), 2.1−1.1 (m, H), 1.11 (s, 3H), 0.84 (s, 3H); $^{13}$C NMR (75.4 MHz): $\delta$ 220.9 ($C_q$), 54.0 ($CH_2$), 52.5 (CH), 52.2 (CH), 37.2 ($C_q$), 29.7 ($CH_2$), 29.5 ($CH_2$), 27.5 ($CH_3$), 27.1 ($CH_2$), 26.9 ($CH_2$), 26.1 ($CH_2$), 25.5 ($CH_2$), 22.2 ($CH_3$). MS (CI): $m/z$ = 195 ([M + 1]$^+$, 3%), 212 ([M + 18]$^+$, 100%), 229 ([M + 35]$^+$, 18%). Conditions for the GC analysys: SE−30 column (30 m × 0.32 mm) isotherm temperature program, He as carrier gas (2.4 mL/min), 165 °C. $t_R$ (**11**) = 16.9 min; $t_R$ (**6**) =17.4 min.

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**Supporting Information Available:** Reagents and quantities used in the preparation of compounds **2**, **4**, **5b**, **6**, **7b**, and **11**; copies of the $^{13}$C NMR spectra of compounds **1**−**11**; HETCOR and NOESY spectra, and tables summarizing the spectral data of compounds **3**, **4**, **7b**, **8**, and **9** (31 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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