

Intermolecular *vs.* Intramolecular Carbene Reactions of a Cage-Functionalized Cyclopentylcarbene

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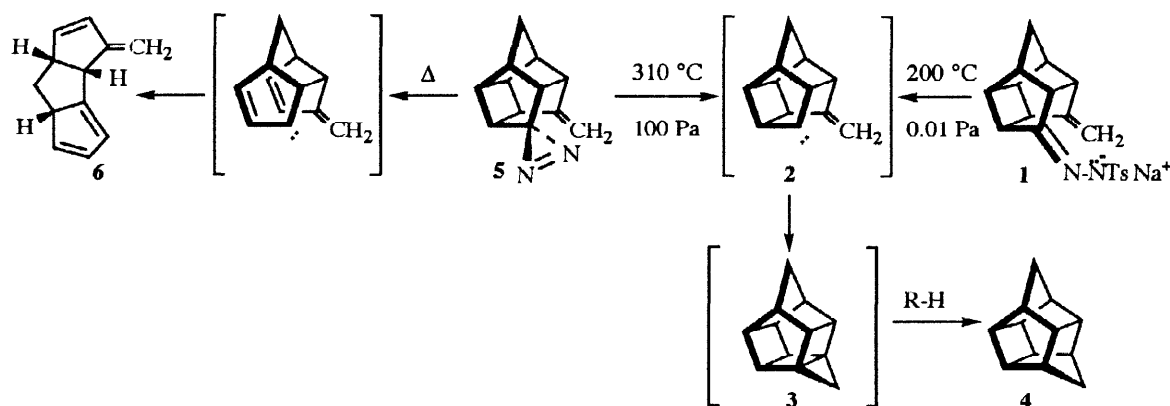
Abstract. The results of carbene reactions of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-ylidene (i.e., PCU-8-ylidene, **9**), generated under different conditions by using different precursors [i. e., (i) sodium salt of PCU-8-one *p*-tosylhydrazone (**8**), (ii) PCU-8-diazirine (**11**), and (iii) 8,8-dibromo-PCU (**12**)], are reported. PCU-8-carbene (**9**), generated thermally from **8**, afforded homopentaprismane (**17**, 9.6% yield) via intramolecular C-H insertion along with other reaction products. By way of contrast, photodecomposition of **11** afforded a mixture of isomeric azines, **21a-21d**, as the major reaction product. No intramolecular carbene trapping products were obtained when **9** was generated via reaction of **12** with *n*-BuLi. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction. The synthesis and chemistry of novel, highly strained, polycarbocyclic "cage" compounds have attracted considerable attention in recent years.¹ Several such compounds can be prepared via inter- or intramolecular addition and/or insertion reactions of corresponding carbene intermediates.^{2,3} Although some aspects of the chemistry of carbenes generated in different media appear to be relatively well understood,⁴ it generally is not possible to predict with certainty the fate of polycyclic cage alkylidenes. Thus, carbene, **2**, generated via pyrolysis of the sodium salt of 11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one tosylhydrazone (i.e., **1**, Scheme 1) has been reported to undergo intramolecular cycloaddition to afford the corresponding [2.2.1]propellane, **3**, which ultimately is reduced *in situ* to produce 1,3-bishomopentaprismane (i.e., **4**, Scheme 1).⁵ By way of contrast, generation of carbene **2** via flash vacuum pyrolysis of the corresponding diazirine (**5**) at high temperature results in the formation of the corresponding cycloadduct, **3**, accompanied by a tricyclic tetraene, **6**, that results via thermal [2 + 2] cycloreversion of **5** followed by loss of N₂ and insertion of the resulting carbene into an adjacent C-H bond.⁵

In order to gain insight into the chemical reactivity of cage-annulated carbenes, a study of the reactions of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-ylidene (**9**, Scheme 2) has been undertaken by employing a variety of experimental conditions. Thus, carbene **9** was generated via three methods: (i) pyrolysis of

the dry Na^+ salt of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one *p*-toluensulfonylhydrazone (i.e., PCU-8-one *p*-tosylhydrazone, **8**) in *vacuo* (ii) photolysis of a benzene solution of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-spiro-3'-diazirine (i.e., PCU-8-diazirine, **11**), and (iii) via reaction of 8,8-dibromopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (i.e., 8,8-dibromo-PCU, **12**) with *n*-BuLi at low temperature.

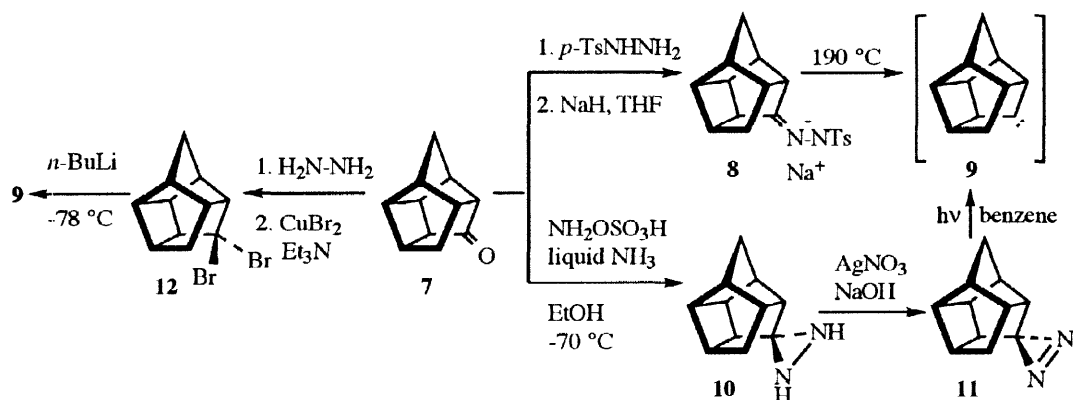
Scheme 1



RESULTS AND DISCUSSION

Preparation of Carbene Precursors. The methods employed to prepare the carbene precursors, i.e., **8**, **11**, and **12**, are shown in Scheme 2. Thus, PCU-8-one (**7**) was converted quantitatively into the corresponding tosylhydrazone sodium salt, **8**, by using a previously published procedure.⁶ Diazirine **11** was prepared in 77% yield via reaction of **7** with freshly prepared hydroxylamine-*O*-sulfonic acid⁷ and liquid ammonia. Oxidation of diaziridine **10** with AgNO_3 ⁸ afforded **11** in 46% yield after column chromatographic purification. 8,8-Dibromo-PCU (**12**) was synthesized by converting **7** into the corresponding hydrazone; subsequently, the hydrazone was allowed to react with $\text{CuBr}_2\cdot\text{NEt}_3$ (see the Experimental Section).⁹

Scheme 2

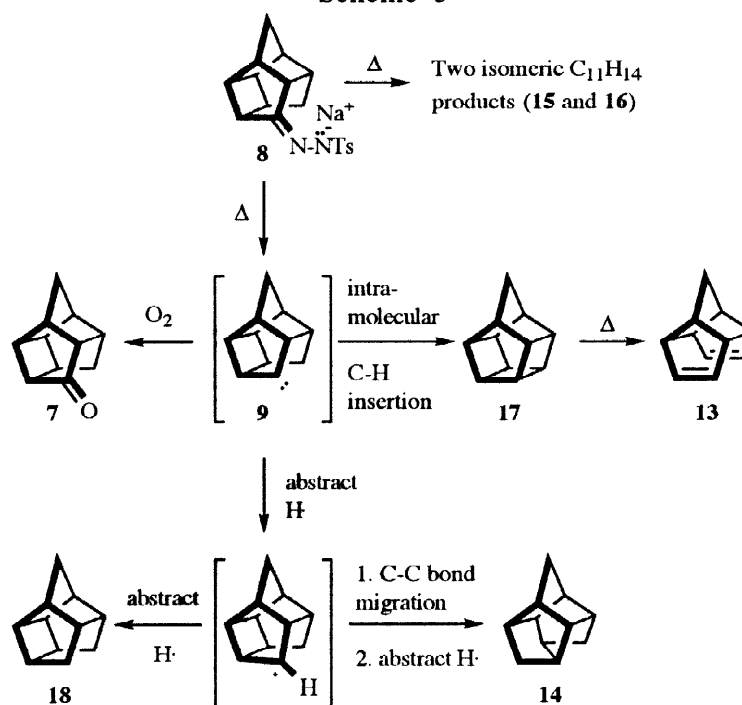


Pyrolysis of 8. Dry **8** was decomposed thermally by heating at 190 °C in *vacuo*. This procedure afforded a mixture of several products (shown in Scheme 3).

The results obtained via pyrolysis of **8** are shown in Table 1.¹⁰ GC-MS analysis was performed by using a 30 m DB-5 capillary column that was operated over the temperature range 60–200 °C. Compounds **13**,¹¹ **14**,¹² **17**,^{11a,c} and **18**,^{12c,13} were separated together (i.e., as a mixture) from ketone **7** and pentacyclo[5.4.0.0^{2,6}.0^{3,10}.

.05,9]undecane-*endo*-8-ol (**19**).¹⁴ Proton and ¹³C NMR spectra of the mixture of **13**, **14**, **17**, and **18** were obtained, and the individual components of this mixture were identified by comparison with the corresponding spectra of authentic samples and also by GC-internal standard. Those components of the product mixture that displayed retention times of 13.10 and 13.20 minutes (i.e., **15** and **16**, respectively) could not be isolated. We conjecture that the formation of ketone **7** and alcohol **19** as products of this reaction might have resulted via reaction of carbene **9** with atmospheric oxygen and/or moisture.

Scheme 3

Table 1. Mixture of products obtained via pyrolysis of **8**.

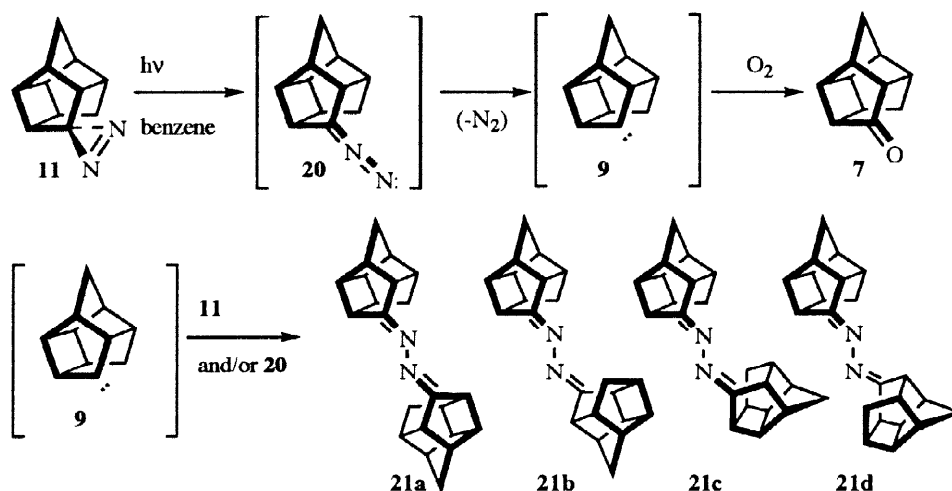
Compound	13	14	15	16	17	18	19	7
GC-MS (M ⁺)	144	146	146	146	144	146	162	160
GC-MS yield (%) ^a	3.1	13.7	6.6	2.7	9.6	2.6	21.0	25.0
GC-retention time (minutes)	12.23	12.50	13.10	13.20	13.78	14.06	18.79	20.48

^aAverage of four pyrolyses.

Photodecomposition of 11. Irradiation of degassed benzene solutions of PCU-8-diazirine (**11**) in Pyrex vessel by using 350 nm radiation produced a mixture of four isomeric azines, i.e., **21a-21d**, along with a small amount of **7** (see Scheme 4). Stevens and coworkers¹⁵ have provided evidence for the formation of diazocycloalkane in the initial phases of the liquid-phase photolysis of spirocycloalkane-functionalized diazirines. Also, the formation of an intermediate, linear diazo-compound has been proposed in connection with the photodecomposition of adamantane-2-spiro-3'-diazirine.¹⁶ The formation of **7** might be ac-

counted for via the reaction of carbene **9** with O₂, which is expected to be present in low concentration in the reaction medium.^{17a} As a control, a non-degassed benzene solution of **11** was irradiated through Pyrex; a mixture of **7** and azines **21a-21d** was obtained (product ratio **7**: **21a-21d** = 3 : 1).^{17b}

Scheme 4



Low-temperature Reaction of **12 with *n*-BuLi.** Reaction of **12** with *n*-BuLi in pentane at -78°C afforded a mixture of five products, i.e., **18** and **22-25** (see Table 2). The product ratios were determined via GC-mass spectral analysis. No intramolecular reaction product was detected, and no intramolecular carbene trapping products were obtained under these conditions. The various reaction products appear to have resulted via organolithium intermediates formed via halogen exchange between **12** and *n*-BuLi and/or via intermolecular insertion of carbene **9** into C-H bonds in the solvent.¹⁸

Table 2. Mixture of products obtained via reaction of **12** with *n*-BuLi in pentane solution at -78°C .

Compound	18	22	23	24	25
GC-MS (M^+)	146	224	303	201 ($M-\text{CH}_3$) ⁺	258
GC-MS yield (%) ^a	14.4	18.4	26.0	9.8	2.4
GC-retention time (minutes)	14.06	28.88 29.19	23.35 24.01	30.05	31.29

^aAverage of three experiments.

Summary and Conclusions. Novel pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCU) derivatives **8**, **11** and **12** have been synthesized via the method shown in Scheme 2. The fate of carbene **9**, generated from **8**, **11** and **12** under different conditions was assessed by GC-Mass analysis. The mode of thermal decomposition of sodium salt **8** is consistent with formation of the corresponding PCU-8-carbene which reacts further via intramolecular C-H bond insertion or via H-abstraction to give a mixture of PCU-hydrocarbons (Scheme 3). However, carbene **9** generated photochemically from diazine **11** afforded a mixture of isomeric azines (**21a-21d**) as the major reaction product. No intramolecular insertion or rearrangement products were formed when **9** was generated by reacting **12** with *n*-BuLi. These results clearly indicate that the fate of carbene **9** depends upon the reaction conditions under which it is generated.

EXPERIMENTAL SECTION

The purity of all compounds was determined by GLC and/or ¹³C NMR spectral analysis. GLC analyses were performed by using a Varian 3300 gas chromatograph equipped with either a DB-210 or a DB-1 capillary column. GC-MS analyses were performed on a Varian-Saturn II GC-mass spectrometer. ¹H and ¹³C NMR spectra were obtained on a Varian Gemini 300 spectrometer. IR spectra were recorded on a Perkin-Elmer M-297 spectrophotometer. UV-spectra were recorded on Philips PU 8730 UV/VIS spectrophotometer. Melting points were determined on a Kofler apparatus and are uncorrected. Elemental microanalyses were performed by personnel at the Central Analytical Laboratory of the Rudjer Bošković Institute, Zagreb, Croatia.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one *p*-Tosylhydrazone. To a solution of *p*-toluenesulfonylhydrazine (595 mg, 3.2 mmol) in absolute EtOH (8 mL) at 80 °C was added **7** (480 mg, 3 mmol) in small portions. The resulting homogeneous mixture was cooled to ambient temperature, whereupon a colorless solid precipitated from solution. The crude product was collected by suction filtration, and the residue was washed with pentane (20 mL). The residue was dried *in vacuo*, thereby affording PCU-8-*p*-tosylhydrazone (984 mg, 100%) as a colorless microcrystalline solid. Recrystallization of this material from CH₃OH afforded analytically pure PCU-8-*p*-tosylhydrazone (obtained as a mixture of *Z,E* isomers) as a colorless microcrystalline solid: mp 174–176 °C; IR (KBr) 3200 (s), 2960 (s), 2860 (m), 1670 (m), 1600 (m), 1330 (s), 1160 (s), 1090 (m), 1010 (m), 930 cm⁻¹ (m); ¹H NMR (CD₃OD) δ 0.85 (AB, *J*_{AB} = 12.5 Hz, 1 H), 0.87 (AB, *J*_{AB} = 12.2 Hz, 1 H), 1.10 (AB, *J*_{AB} = 12.5 Hz, 1 H), 1.12 (AB, *J*_{AB} = 12.2 Hz, 1 H), 1.29 (AB, *J*_{AB} = 9.8 Hz, 1 H), 1.32 (d, *J* = 9.5 Hz, 1 H), 1.68 (d, *J* = 9.8 Hz, 1 H), 1.71 (d, *J* = 9.5 Hz, 1 H), 2.10–2.80 (m, which contains a discernible singlet at δ 2.30, 22 H), 3.21 (br s, 2 H), 7.25 (d, *J* = 7.9 Hz, 4 H), 7.66 (d, *J* = 7.9 Hz, 4 H); ¹³C NMR (CD₃OD) δ 21.7 (q), 31.8 (t), 32.1 (t), 37.2 (t), 37.5 (t), 37.6 (d), 40.3 (d), 40.9 (d), 41.1 (d), 41.7 (d), 43.1 (d), 44.4 (d), 44.6 (d), 45.3 (d), 45.9 (d), 47.2 (d), 47.7 (d), 48.8 (d, 2 C), 48.9 (d), 50.5 (d), 129.3 (d), 130.9 (d), 138.0 (s), 145.5 (s), 173.2 (s), 173.8 (s). Anal. Calcd. for C₁₈H₂₀N₂O₂S: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.84; H, 6.25; N, 8.54.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one Tosylhydrazone Sodium Salt (8**).** Sodium hydride (50% suspension in mineral oil, 0.160 g, 3.2 mmol) was added in small portions with stirring to a solution of PCU-8-*p*-tosylhydrazone (984 mg, 3.0 mmol) in dry THF (10 mL) at ambient temperature. After all of the NaH had been added, the resulting thick suspension was stirred at ambient temperature for an additional 1 h. The reaction mixture was concentrated *in vacuo*, and the residue (crude **8**) was dried *in vacuo* (10⁻³ mm Hg, 40 °C) for 2 h prior to use.

Pyrolysis of **8.** A reaction flask that contained dry **8** (525 mg, 1.5 mmol) was connected to a high-vacuum line through an in-line "U" trap. The trap was cooled via immersion in a liquid N₂ cold bath, and the resulting pyrolysis system was evacuated to 5 × 10⁻⁴ mm Hg. The reaction flask was immersed in an external hot oil bath (210 °C), and the system was maintained at 190 °C for 20 minutes to complete the pyrolysis of **8**. The oil bath was removed, and the apparatus was pressurized to 1 atmosphere with dry N₂. The product that had collected in the cold trap (45 mg, 0.3 mmol, 20%) was dissolved in C₆D₆ (0.5 mL), and the resulting solution was

subjected to ^{13}C NMR spectral and glc analysis; the results thereby obtained appear in Table 1. The hydrocarbon products were separated from ketone **7** and alcohol **19** via column chromatography on silica gel. Pentane elution afforded a mixture of hydrocarbons (19 mg). Continued elution of the chromatography column with Et_2O afforded **7** (12 mg). Finally, continued elution of the chromatography column with 5% $\text{MeOH-Et}_2\text{O}$ afforded **19** (10 mg). Authentic **19** was synthesized independently (*vide infra*).

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-spiro-3'-diazirine (11). A solution of **7** (240 mg, 1.5 mmol) in absolute EtOH (4.5 mL) was cooled to -70°C via application of an external dry ice-acetone cold bath. To this cooled solution was added dropwise with stirring liquid NH_3 (ca. 20 mL, excess). After all of the liquid NH_3 had been added, the resulting mixture was stirred at -70°C for 40 minutes. To the reaction mixture was added with stirring a solution of freshly prepared hydroxylamine-*O*-sulfonic acid (340 mg, 3.0 mmol) in MeOH (2 mL), and the resulting mixture was stirred at -70°C for 3 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into water (20 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried (MgSO_4) and filtered, and the filtrate was concentrated *in vacuo*. Crude **10** (256 mg, 98%) was thereby obtained; IR (KBr) 3200 (s), 2950 (s), 2860 (m), 2210 (w), 1450 (w), 1410 (w), 1310 (w), 1300 (w), 1270 (w), 1170 (w), 1150 (w), 1030 (w), 910 cm^{-1} (m). This material was used as obtained in the next synthetic step, without additional purification or characterization.

To a solution of crude **10** (256 mg, 1.47 mmol) in CH_3OH (10 mL) was added sequentially 1 N aqueous AgNO_3 (2.5 mL, 2.5 mmol) followed by dropwise addition of 2.5 N aqueous NaOH (1 mL, 2.5 mmol). The resulting mixture was stirred at ambient temperature for 15 minutes and then was filtered. Water (50 mL) was added to the filtrate, and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried (MgSO_4) and filtered, and the filtrate was concentrated *in vacuo*, thereby affording crude **11** (200 mg, 79%). This material was further purified via column chromatography on alumina (activity grade II/III) by eluting with pentane. Pure **11** (116 mg, 46%) was thereby obtained as a colorless waxy solid: UV (EtOH) $(\lambda_{\text{max}})_1 = 354.0\text{ nm}$ ($\epsilon = 322$), $(\lambda_{\text{max}})_2 = 371.7\text{ nm}$ ($\epsilon = 327$); IR (KBr) 2950 (s), 2860 (m), 1580 (m), 1450 (w), 1310 (w), 1270 cm^{-1} (w); ^1H NMR (CDCl_3) δ 1.10–1.60 (m, 4 H, with a discernible doublet at δ 1.33, $J = 10.5\text{ Hz}$), 1.67 (d, 1 H, $J = 10.5\text{ Hz}$), 2.30–2.90 (m, 7 H); ^{13}C NMR (CDCl_3) δ 29.7 (t), 35.0 (t), 37.1 (d), 37.8 (s), 38.9 (d), 41.0 (d), 42.7 (d), 43.5 (d), 43.8 (d), 45.8 (d), 47.4 (d). HRMS for $\text{C}_{11}\text{H}_{12}\text{N}_2$ Calcd M_r^+ 172.100048. Found: M_r^+ 172.099623.

Photolysis of 11. A solution of **11** (111 mg, 0.64 mmol) in benzene (1 mL) was placed in a Pyrex tube. A stream of N_2 was passed through this solution during 0.5 h to purge O_2 from the solution. The resulting solution was irradiated in a Rayonet reactor equipped with sixteen 350 nm lamps during 1 h. The reaction mixture then was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by using a 0–20% $\text{EtOAc-CH}_2\text{Cl}_2$ gradient elution scheme. The first chromatography fraction obtained by eluting the column with pure CH_2Cl_2 afforded **7** (13 mg, 12%). Subsequent elution with 20% $\text{EtOAc-CH}_2\text{Cl}_2$ afforded a mixture of isomeric azines, **21a–21d** (58 mg, 57%) as a colorless microcrystalline solid: UV (EtOH) $\lambda_{\text{max}} = 234\text{ nm}$ ($\epsilon = 8840$); IR (KBr) 2950 (s), 2860 (w), 1670 (s), 1450 (w), 1310 (vw), 1300 cm^{-1} (vw); ^1H NMR (C_6D_6) δ 1.00–1.25 (m, 2 H), 1.30–1.70 (m, 2 H), 2.00–3.10 (m, 7 H), 3.70–4.16 (m, 1 H); ^{13}C NMR (C_6D_6) δ 31.52 (t), 31.59 (t), 31.74 (t), 31.83 (t), 36.67 (t), 36.72 (t), 36.89 (t), 36.95 (t), 39.29 (d), 39.36 (d), 39.41 (d), 39.76 (d), 39.84 (d), 39.92 (d), 39.98 (d), 40.64 (d), 42.10 (d), 42.15 (d), 43.56 (d), 43.69 (d), 43.75 (d), 44.01 (d), 44.05 (d), 44.09 (d), 44.19 (d), 44.64 (d), 44.81 (d), 44.88 (d), 45.65 (d), 45.81 (d), 46.68 (d), 46.76 (d), 47.67 (d), 47.87 (d), 48.02 (d), 48.07 (d), 49.34 (d), 49.45 (d), 49.49 (d), 49.54 (d), 175.55 (s), 175.72 (s), 175.84 (s), 175.90 (s). Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.35; H, 7.63; N, 8.82.

8,8-Dibromopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (12). The procedure described by Takeda *et al.*⁹ was employed to prepare **12**. Thus, to a suspension of finely powdered molecular sieves (4 Å, 4.00 g) in dry MeOH (15 mL) was added with stirring **7** (610 mg, 3.81 mmol) and anhydrous hydrazine (2.44 g, 76.3 mmol), and the resulting mixture was stirred at 25°C for 3 h. The reaction mixture was filtered, and the

residue was washed with ether (20 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue, PCU-8-one hydrazone, was used as obtained in the next synthetic step without further purification or characterization.

A solution of CuBr₂ (4.01 g, 18.0 mmol) in dry MeOH (25 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring Et₃N (910 mg, 9.0 mmol) during 5 minutes. After addition of Et₃N had been completed, the reaction mixture was allowed to stir at 0 °C for an additional 20 minutes. To this mixture was added dropwise with stirring a solution of crude PCU-8-one hydrazone that had been obtained previously (*vide supra*) in MeOH (6 mL). The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 2 h. The reaction was quenched via addition of 10% aqueous NH₄OH (50 mL), and the resulting deep blue aqueous solution was extracted with Et₂O (4 x 25 mL). The combined organic layers were washed with water (20 mL), dried (MgSO₄), and filtered, and the filtrate was concentrated *in vacuo*. The oily residue thereby obtained was distilled *in vacuo* to afford pure **12** (870 mg, 76%) as a colorless oil: bp 178 °C (0.5 mm Hg); IR (neat) 2987 (s), 1480 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.22 (AB, *J*_{AB} = 10.2 Hz, 1 H), 1.73 (AB, *J*_{AB} = 10.2 Hz, 1 H), 2.40–3.31 (m, 10 H); ¹³C NMR (CDCl₃) δ 26.6 (t), 31.9 (t), 30.8 (d), 40.5 (d), 43.4 (d), 44.4 (d), 47.8 (d), 49.0 (d), 51.8 (d), 58.1 (d), 72.0 (s). Anal. Calcd for C₁₁H₁₂Br₂: C, 43.46; H, 3.98. Found: C, 43.37; H, 4.03.

Reaction of **12 with *n*-BuLi.** A solution of **12** (410 mg, 1.27 mmol) in dry pentane (10 mL) was cooled to -78 °C via application of an external dry ice-acetone bath. To this cold solution was added dropwise with stirring a solution of *n*-BuLi in pentane (2.0 M, 1.9 mL, 3.80 mmol) during 10 minutes. After all of the *n*-BuLi had been added, the resulting mixture was stirred at -78 °C for 2 h. The external cold bath then was removed, and the reaction mixture was allowed to warm gradually to ambient temperature during 2 h. Excess *n*-BuLi was quenched via dropwise addition of cold water (10 drops), and the resulting mixture was dried (MgSO₄) and filtered. The filtrate was analyzed by GC-Mass (capillary column DB-5, 30 m, 60–200 °C; see Table 2).¹⁸

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-*endo*-8-ol (19**).** A solution of **7** (112 mg, 0.70 mmol) in dry Et₂O (10 mL) at ambient temperature was added dropwise with stirring to a suspension of LiAlH₄ (30 mg, 0.80 mmol) in dry Et₂O (2 mL), and the resulting mixture was refluxed with stirring for 4 h. Work-up of the reaction mixture by using standard procedures afforded **19** (109 mg, 96%) as a colorless microcrystalline solid: mp 192–195 °C [lit.^{14a} mp 180–185 °C (for a 1 : 1 isomeric mixture of PCU-*exo*-8-ol and PCU-*endo*-8-ol); lit.^{14b} mp 231–232 °C (for isomerically pure PCU-*endo*-8-ol); lit.^{14c} mp 209–211 °C (for optically active (-)-PCU-*endo*-8-ol)]; IR (KBr) 3280 (s), 2950 (s), 2860 (w), 1450 (vw), 1350 (w), 1260 (m), 1170 (w), 1090 (w), 1070 cm⁻¹ (m); ¹H NMR (C₆D₆) δ 1.00–1.20 (m, 2 H), 1.25 (br s, 1 H), 1.63 (d, *J* = 10.4 Hz, 1 H), 2.00–2.80 (m, 9 H), 3.66 (br s, 1 H); ¹³C NMR (C₆D₆) δ 29.0 (t), 35.5 (t), 36.6 (d), 39.3 (d), 40.2 (d), 42.4 (d), 42.6 (d), 43.4 (d), 46.1 (d), 47.4 (d), 74.2 (d).

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17. (a) Reaction of diadamantylcarbene with oxygen: Morgan, S.; Platz, M. S.; Jones, M. Jr.; Myers, D. R. *J. Org. Chem.* **1991**, *56*, 1351-1353. (b) Similarly, photolysis of adamantane-2-spiro-3'-diazirine in benzene solution afforded azines and 2-adamantanone (product ratio 1.25 : 1, respectively); see: Isaev, S. D.; Sherstyuk, V. P.; Kozlov, O. F.; Skripkin, V. V.; Yanku, I. *Teor. Eksp. Khim.* **1991**, *27*, 211-220.
18. When this reaction was performed in THF, the product that resulted via insertion of carbene **9** into a C-H bond of THF was present in the reaction mixture. The ratio of products varied from one experiment to another; the variation in yield of **18** was particularly notable, most likely due to its high volatility.