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Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1-ene: Formation and Trapping of 1,2-Dehydroquadricyclane. Ab Initio Calculations on Dehydroquadricyclanes

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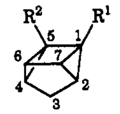
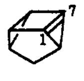
Hydrogen chloride elimination from chloroquadicyclane 14 with *tert*-butyllithium or *n*-butyllithium/potassium *tert*-butoxide in ether at 0 °C led to the title compound 4 as a reactive intermediate. Generating 4 with LDA in the presence of diphenylisobenzofuran (8) or trimethylisoindole (9) afforded the Diels–Alder adducts **18a** and **19a**. Ab initio calculations at the TCSCF/6-31G* level have been performed on the dehydroquadricyclanes 2–7, and total energies and olefinic strain energies have been determined for those molecules.

The rigid carbon framework of quadricyclane (tetrahydro[3.2.0.0^{2,7}.0^{4,6}]heptane) (**1a**) and its facile accessibility[1] make this hydrocarbon a suitable system for research aiming to place CC double bonds at unusual positions.[2] More than a decade ago it was shown that **1a** could be metalated at C-1 by a mixture of butyllithium (BuLi)/potassium *tert*-butoxide (KO-*t*-Bu) or by the complex of BuLi and tetramethylethylendiamine (TMEDA) and that the intermediate **1c** could be easily functionalized at this position. Treatment of 1-chloroquadricyclane (**1b**) with strong bases in the presence of reactive 1,3-dienes led to Diels–Alder adducts which showed that 1,7-dehydroquadricyclane (**2**) had been trapped.[3] Some years ago it was demonstrated that 1-bromo-5-chloroquadricyclane (**1d**) on treatment with *t*-BuLi at low temperatures in the presence of diphenylisobenzofuran (DPIBF, **8**), 1,2,3-trimethylisoindole (**9**), or 2,5-dimethylfuran (**10**) produced adducts of the short-lived 1,5-dehydroquadricyclane (**3**).[4] In this paper we report results of experiments toward the generation of 1,2-dehydroquadricyclane (**4**), the third (mainly) pyramidalized olefin within the quadricyclane carbon framework. It should be mentioned that the 1,2-dehydroquadricyclane skeleton has been suggested as a fleeting intermediate in some derivatives carrying substituents at C-3[5] or at C-6 and C-7.[6] In addition to our experimental investigations, we performed ab initio MO calculations on dehydroquadricyclanes **2–7** to obtain information on their heats of formation.



1	a	b	c	d
R^1	H	Cl	Li	Br
R^2	H	H	H	Cl



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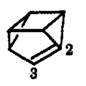

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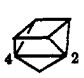

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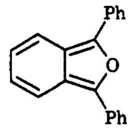

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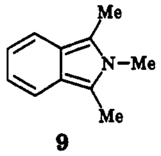

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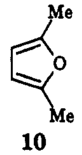

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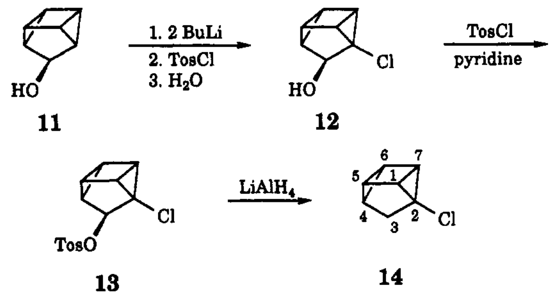
Scheme I



Results and Discussion

Synthesis of the Precursor. 2-Chloroquadricyclane (**14**), from which **4** could be generated by metalation of C-1 and elimination of lithium chloride, was synthesized using 3-quadricyclanol (**11**), which is accessable from norbornadiene in four steps.[7,8] Metalation of **11** with 2 equiv of BuLi and reaction with tosyl chloride led to a mixture of two chlorides **12** and **15** in a 5.7:1 ratio, which could not be separated by fractional distillation. Tosylation of the mixture of isomers with tosyl chloride in pyridine gave **13** and **16**. Recrystallization from pentane resulted in almost pure **13** (ratio greater than 20:1), leaving the side product **16** in the mother liquor.

Reduction of **13** with lithium aluminum hydride in ether led to the chloride **14** in an overall yield of 4.4% (see Scheme I).

The kinetic acidity of hydrogen atoms in alicyclic hydrocarbons can be related to the corresponding ^{1}H–^{13}C coupling constants.[9] Table I shows the ^{13}C–^{1}H coupling

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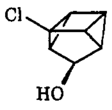
Table I. ^1H–^{13}C Coupling constants of 14

atom position	$^1J_{^1H-^{13}C}$ (Hz)	atom position	$^1J_{^1H-^{13}C}$ (Hz)
C-1, C-7	188	C-4	169
C-5, C-6	186	C-3	135

constants of chloride 14. The value for C-1 and C-7 is only slightly higher than the one for C-5 and C-6. However, additional directing effects of the chlorine atom at C-2 ensure a specific attack of the base at C-1 and C-7.



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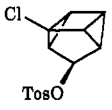

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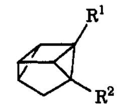
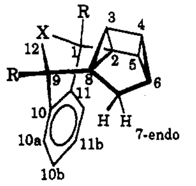
Deprotonation of 14 with an excess of *tert*-butyllithium (*t*-BuLi) and aqueous workup led to a mixture of 1-*tert*-butylquadricyclane **17a** and a product, the ^{13}C NMR signals of which could in part be assigned to the *cine* substitution product 2-*tert*-butylquadricyclane **17b**. Reaction of 14 with an excess of BuLi/KO-*t*-Bu afforded the *n*-butyl-substituted quadricyclanes **17c** and **17d**, respectively. An obvious explanation for the formation of the product mixtures is the assumption that **4** is formed as an intermediate, generated by lithium chloride elimination of the metalated quadricyclanes **17e** and **17f**.

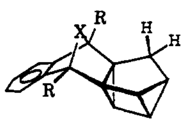


17	a	b	c	d	e	f
R^1	*t*-Bu	H	Bu	H	Li	K
R^2	H	*t*-Bu	H	Bu	Cl	Cl

When the metalation of 14 was carried out with the less nucleophilic LDA, the intermediate **4** could be trapped with some reactive dienes as a Diels–Alder adduct. In the presence of **8** or **9** the [3.3.1]propellanes **18** and **19** were formed. Each of these trapping reactions could lead to two isomers (**18a/b**, **19a/b**). In both cases only one of the stereoisomers was found in the NMR spectra of the crude product. The structure of **18** was determined by single-crystal X-ray analysis, showing that the isomer **18a** had been obtained.[31] The NMR spectra of **18a** including NOESY and HETCOR spectra are in accordance with this structure. For **19**, NOESY and HETCOR spectra favor the *endo*-structure **19a** as well. Specifically, in the ^1H-NMR spectra of **19a**, the protons at positions C-7 appear at δ 0.94 and 1.79. The upfield shift of the *endo* proton seems to be caused by anisotropic interaction with the fused benzene ring. Molecular models[10] show that this interaction is to be expected only for the *endo* isomer **19a**.



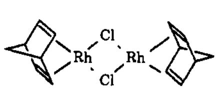
a



b

	18	19
X	O	N-Me
R	Ph	Me

The rearrangement of quadricyclanes to the corresponding norbornadienes is catalyzed inter alia by iodine[11] and several transition metal complexes.[12] One of the most commonly used catalysts seems to be di-μ-chlorobis(bicyclohepta-2,5-diene)dirhodium (**20**).[13] A solution of **18a** with 10 mol % of catalyst **20** was monitored by ^1H NMR spectroscopy. New signals at δ 6.25 and 6.59 appeared which were assigned to norbornadiene **21**. After 12 days at room temperature, the signals of **18a** had completely disappeared. The resulting norbornadiene **21** contains a *trans*-cyclooctene ring, for which stability at room temperature is to be expected according to the principle of Wiseman.[14] Attempts at further purification led to polymerization of **21**. The olefinic bridgehead carbon shows a chemical shift of 164.5 ppm, which should be caused by torsional effects of the CC double bond in **21**.[15]



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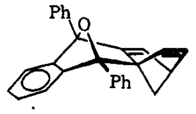

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Ab Initio Calculations. The determination of the heats of formation of reactive intermediates like the dehydroquadricylanes cannot be achieved by classical methods. In this case ab initio MO calculations may contribute additional information on the properties of such molecules: relative heats of formation, olefinic strain energies, and structural data of the short-lived intermediates were our points of interest. Calculations have been carried out on the already trapped dehydroquadricyclanes **2**–**4**; supplementary calculations have been performed on the yet unknown isomers **5**–**7**.

All geometries were optimized with the 6-31G* basis set[16] within the restriction of their symmetries. Due to the diradical character expected in **2**–**7**,[17] two-configuration (TC) SCF wave functions were employed,[18] using the GVB option in Gaussian 90.[19] The relative TCSCF energies are given in Table II. Also listed for comparison are the ROHF energies[20] of the lowest triplet states for **2**–**7**, optimized with the 6-31G* basis set.

Table II shows that the differences of the singlet states of **2**–**7** are rather small; this suggests that **5**–**7** can probably be generated by the same type of reaction (elimination of metal halide from the precursor). The TCSCF energy of **2** is 11.8 kcal/mol lower than the energy of **3**. A similar result has been reported by Paquette, Borden, *et al.*, who

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[10] PCMODEL, Molecular Modeling Software, Serena Software, Bloomington, IN.

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Table II. Relative Energies (kcal/mol) of the Lowest Singlet and Triplet States of 2–7 at Geometries[a] Optimized with the 6-31G* Basis Set

molecule[b]	6-31G* TCSCF singlet	6-31G* ROHF triplet
2	0.0[c]	21.9
4	4.0	34.0
3	11.8	26.0
6	12.1	26.9
7	12.7	24.9
5	14.5	14.7

[a] TCSCF geometries for singlets and ROHF geometries for triplets. [b] In order of increasing energy. [c] $E = -268.3537$ hartrees.

found prismene **22** to be more stable by 10.4 kcal/mol than prismene **23**.[21] The energy of **4**, the third (mainly) pyramidalized isomer, is 4.0 kcal/mol higher than the energy of **2**. The ratios of the squares of the two coefficients in the TCSCF wave function of **2**, **4**, and **3** are 8.51, 7.55, and 5.90, respectively, indicating an increasing diradical character in this order.[22] The C–C distances of the double bonds are 1.371, 1.366, and 1.429 Å for **2**, **4**, and **3**, respectively. The olefinic strain energies[23] are computed relative to bicyclo[3.3.1]oct-1(5)ene (**24**), which has served as the reference alkene in the OSE calculations reported by Hrovat and Borden.[21a,24] The OSEs for **2**, **4**, and **3** are 67, 71, and 79 kcal/mol. To our knowledge, the latter is the highest value computed for a bridgehead alkene for which at least some experimental evidence for existence has been provided.

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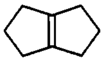

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The energy of **5**, the fourth olefin in this series, is only 14.5 kcal/mol higher than the energy of **2**, although the overlap of the 2p orbitals seems to be very low. Actually, the ratio of the squares of the two coefficients of the TCSCF wave function is only 2.31, which can be transformed to a diradical character of 60%.[25] The bond distance of the C2–C3 double bond is 1.444 Å, which shows a tendency toward a C–C single bond. Whereas the singlet–triplet gaps for **2**, **3**, and **4**, given in Table II, are greater than 14.2 kcal/mol, the triplet energy of **5** is only 0.2 kcal/mol higher than the corresponding singlet energy. All these parameters indicate a very low interaction between the 2p orbitals at C-2 and C-3. However, some overlap is retained by pyramidalization of C-3: the structure of **5** around the C–C double bond distorted such that the hydrogen atom at C-3 is inclined to the plane formed by C-2, C-3, and C-4 by an angle of 47°. A polarization of the double bond, placing a negative partial charge at C-2 and a positive one at C-3 as proposed for related compounds,[26] does not seem to play an important role: the charge difference of C-3 and C-2 was computed to be only 0.13 e. At 81 kcal/mol the OSE for **5** is even higher than for **3**.

The energy difference of [2.2.1]propellane (**6**) and [3.1.1]propellane (**7**) is 0.6 kcal/mol only. However, the diradical character of these two molecules differs considerably: The ratio of the squares of the coefficients in the TCSCF wave function are 3.99 (for **6**) and 6.10 (for **7**), respectively. The difference in diradical character between **6** and **7** is reflected in the difference of bonds C2–C4 in **6** and C1–C6 in **7**: the distance is calculated to be 2.123 Å, the other one 1.908 Å. The singlet–triplet gaps for **6** and **7** are rather similar (14.8 and 12.2 kcal/mol).

The data on the dehydroquadricyclanes from ab initio calculation are in accordance with the experimental results obtained so far. The three isomers **2**–**4**, which could be trapped by Diels–Alder reactions, have the lowest energies in this series. However, the energies of **5**–**7** are only slightly higher, which might justify the assumption that these molecules could also be generated as fleeting intermediates, provided the appropriate precursors were available.

Experimental Section

The following instruments were used: a Varian VXR 400S NMR spectrometer, a Bruker IR-IFS 45 IR spectrometer, a Zeiss DMR 10 UV spectrometer, and a Finnigan MAT 90 mass spectrometer. Melting points are not corrected. Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol (**11**) was prepared by the methods of Story[7] and Gassman and Patton.[8] 1,3-Diphenylisobenzofuran (**8**),[27] 1,2,3-trimethylisoindole (**9**),[28] and di-μ-chlorobis(bicyclohepta-2,5-diene)dirhodium (**20**)[13] were prepared according to the literature. LDA was prepared as described previously.[29] *n*-Butyllithium (BuLi) was obtained by CHEMETALL AG, Frankfurt, Germany, as a 1.6 N solution in hexane. *tert*-Butyllithium (*t*-BuLi) was purchased from Janssen Chimica as a 1.5 N solution in pentane; its content was determined prior to use by the method of Lipton.[30] All operations with moisture- and air-sensitive compounds were carried out in flame-dried flasks under nitrogen atmosphere. Ether was distilled from lithium aluminum hydride prior to use.

2-Chlorotetracyclo[3.2.0.0^{2,7}.^{4,6}]heptan-3-ol (12). Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol (**11**) (27.43 g, 253 mmol) was dissolved in ether (250 mL) at 0 °C, and BuLi (331 mL, 530 mmol) was added dropwise. After the solution was stirred for 16 h at room temperature, *p*-toluenesulfonyl chloride (78.01 g, 409 mmol, recyrstallized from petrol ether by use of activated charcoal) was added in portions at 0 °C. The solution was stirred for another 2 h at room temperature, hydrolyzed with water (50 mL), and extracted with ether (2 × 50 mL). The ether layers were subsequently treated with 2 N HCl (50 mL), 2 N NaOH (50 mL), and water (50 mL), dried with anhydrous magnesium sulfate ($MgSO_4$), and filtered. The solvent was removed under reduced pressure, and the residue was distilled at 54–56 °C/4 × 10^{-4} Torr, yielding **12** (9.01 g, 25%) as a yellowish liquid, which contained about 15% *syn*-1-chlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol (**15**) (content of **12** and **15** determined by comparison of equivalent ^{13}C NMR signals): IR (neat) 3353, 3077, 2927, 817, 799, 768, 745; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50, 1.83, 2.00–2.06 (m, 5 H, 1-H, 4-H, 5-H, 6-H, 7-H in unknown order), 2.10 (s, variable, 1 H, OH), 4.78 (s, 1 H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.65, 20.02, 24.58, 24.90, 27.03 (d, C-1, C-4, C-5, C-6, C-7 in unknown order), 52.62 (s, C-2), 79.29 (d, C-3); MS (70 eV) *m/e* 141 (M^+, 6), 125 (6), 79 (67), 77 (100); HRMS calcd for $C_7H_6{}^{35}ClO$ 141.011 found 140.996. Anal. Calcd for C_7H_6ClO: C, 58.97; H, 4.95. Found: C, 60.23; H, 5.56.

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2-Chlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-3-yl *p*-Toluenesulfonate (13). *p*-Toluenesulfonyl chloride (13.3 g, 69.5 mmol) was slowly added to a solution of **12** (9.01 g, 63.2 mmol) in anhydrous pyridine (70 mL) at 0 °C. After the solution was stirred for 48 h, water (30 mL) was added at 0 °C and the solution was extracted with cold ether (ice bath, 3 × 30 mL). The organic layers were subsequently washed with ice–water (3 × 30 mL), saturated $NaHCO_3$ solution (2 × 30 mL), and ice–water (30 mL), dried with $MgSO_4$, and filtered. The solvent and traces of pyridine were removed under reduced pressure. Recrystallization from pentane yielded **13** (6.37 g, 34%): mp 48–50 °C; IR (KBr) 1364, 1177, 847, 815, 668, 573; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.60, 1.87, 1.95, 2.07, 2.11 (m, 5 H, H-1, 4-H, 5-H, 6-H, 7-H in unknown order), 2.45 (s, 3 H, CH_3), 5.34 (d, ^3J = 1.8 Hz, 1 H, H-3), 7.36, 7.91 (d, 4 H, 2′-H, 3′-H, 5′-H, 6′-H in unknown order); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.27, 21.00, 23.79, 25.39, 26.02, (d, C-1, C-4, C-5, C-6, C-7 in unknown order), 21.66 (q, CH_3), 48.71 (s, C-2), 88.26 (d, C-3), 128.08, 129.77 (d, C-2′, C-3′ in unknown order), 133.96, 144.78 (s, C-1′, C-4′ in unknown order); MS (70 eV) *m/z* 155 (41), 141 (16), 125 (28), 91 (100), 77 (44), 65 (15). Anal. Calcd for $C_{14}H_{13}ClO_3S$: C, 56.66; H, 4.42; S, 10.81; Cl, 11.95. Found: C, 57.06; H, 4.59; S, 10.86; Cl, 12.45.

2-Chlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (14). **13** (10.3 g, 34.8 mmol) and lithium aluminum hydride (531 mg, 14.0 mmol) were dissolved in anhydrous ether (75 mL) and refluxed and stirred for 20 h. Subsequently, water (0.53 mL), aqueous sodium hydroxide (0.53 mL of 15% solution), and water (1.59 mL) were added at 0 °C. The precipitate was filtered and washed with ether. The filtrate was washed with water (50 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure. Distillation of the residue at 45–46 °C/14 Torr yielded **14** (2.30 g, 52%): IR (neat) 3076, 2938, 2865, 1263, 1227, 810, 788, 729; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37 (tt, ^3J = 1.5, 4.9 Hz, 1 H, 4-H), 1.78 (dt, ^3J = 4.9, 2.2 Hz, 2 H, 5-H, 6-H), 1.84 (t, ^3J = 2.2 Hz, 2 H, 1-H, 7-H), 2.44 (d, ^3J = 1.5 Hz, 2-H, 3-H_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.42 (d, ^1J = 186 Hz, C-5, C-6), 22.17 (d, ^1J = 169 Hz, C-4), 24.70 (d, ^1J = 188 Hz, C-1, C-7), 37.73 (t, ^1J = 135 Hz, C-3), 48.18 (s, C-2); MS (70 eV) *m/z* 126 (M^+, 7), 100 (18), 91 (100), 65 (27); HRMS calcd for $C_7H_7{}^{35}Cl$ 126.024, found 126.012. Anal. Calcd for C_7H_7Cl: C, 66.42; H, 5.57. Found: C, 68.08; H, 5.68.

Generating and Trapping of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1-ene (4) with *t*-BuLi. *t*-BuLi (3.20 mL, 4.80 mmol) was added at 0 °C to a solution of **14** (150 mg, 1.18 mmol) in ether (5 mL). After being stirred for 1 h, the mixture was hydrolyzed with water (5 mL) and extracted with ether (2 × 5 mL). The organic layers were washed with water (2 × 5 mL), dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The residue was flash distilled at 80 °C (bath)/14 Torr and condensed in a dry ice trap. The ^{13}C NMR spectrum of the colorless oil showed signals of the known 1-*tert*-butyltricyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**17a**)[11] and, in addition, signals which could in part be assigned to 2-*tert*-butyltricyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**17b**). Further signals of moderate intensity showed that some impurities were present, the structure of which could not be elucidated.

Generating and Trapping of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1-ene (4) with BuLi/Potassium *tert*-Butoxide. **14** (150 mg, 1.18 mmol) in ether (5 mL) and BuLi (3.00 mL, 4.80 mmol) were added to a solution of potassium *tert*-butoxide (539 mg, 4.80 mmol) in ether (5 mL) at 0 °C. After the solution was stirred for 1 h, water (5 mL) was added and the solution was extracted with ether (2 × 5 mL). The organic layers were washed with water (2 × 5 mL), dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The residue was flash-distilled at 110 °C (bath)/14 Torr and condensed in a dry ice trap. The oily liquid (50 mg) was analyzed by ^{13}C NMR spectroscopy. The ratio of 1-*n*-butyltricyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**17c**) and 2-*n*-butyltricyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**17d**) was 1:1.3. The ^{13}C NMR spectral data for **17c** are known from the literature.[11] The data for **17d**: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.12 (q, C-4′), 16.46 (d, C-5, C-6), 21.62 (d, C-1, C-7), 23.11, 23.41, 29.17, 30.19 (t, C-3, C-1′, C-2′, C-3′ in unknown order), 24.05 (d, C-4) (C-2 covered by background noise).

Generating and Trapping of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1-ene (4) with 1,3-Diphenylisobenzofuran (8). **14** (2.00 g, 15.8 mmol) in THF (20 mL) was added at 0 °C to a mixture of LDA (19.0 mmol) and **8** (5.41 g, 20.0 mmol) in anhydrous THF (20 mL). After being sitrred for 24 h, the mixture was hydrolyzed with water (20 mL) and extracted with ether (2 × 20 mL). The organic layers were washed with water (20 mL), dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The crude fluorescent oil was dissolved in THF (20 mL) and added to a solution of maleic anhydride (1.96 g, 20.0 mmol) and triethylamine (6.07 g, 60.0 mmol) in ether/THF (1:1, 50 mL). After being stirred for 30 min the solution was added to 2 N NaOH (100 mL) in a separating funnel and intensively shaken. The yellowish solution was extracted with ether (3 × 20 mL), the organic layers were washed with water (2 × 20 mL), dried with $MgSO_4$, and filtered, and the solvents were removed under reduced pressure. Evaporation at 50 °C (bath)/4 × 10^{-4} Torr gave **18a** as an almost pure yellowish solid (3.81 g, 67%), which melted after recrystallization from acetonitrile at 147–149 °C: IR (KBr) 3065, 3031, 2917, 1455, 1447, 1304, 773, 765, 753; UV ($CHCl_3$) λ_{max} (log ϵ) 287 (4.08), 275 (4.07), 262 (4.02); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (dd, ^2J = 11.0 Hz, ^3J = 1.1 Hz, NOE at δ 1.60, 2.16, 1 H, 7_{endo}-H), 1.60 (t, ^3J = 4.6 Hz, NOE at δ 1.89, 2.16, 1 H, 6-H), 1.89 (m, NOE at δ 2.16, 7.82, 2 H, 4-H, 5-H), 2.16 (dd, ^2J = 11.0 Hz, NOE at δ 7.67, 1 H, 7_{exo}-H), 3.12 (m, NOE at δ = 7.67, 1 H, 3-H), 6.98–7.01, 7.08–7.12 (m, 4 H, NOE at δ 7.67, 7.82, 4 H, 10a-H, 10b-H, 11a-H, 11b-H in unknown order), 7.13–7.16, 7.35–7.50 (m, NOE at δ = 7.67, 7.82, 6 H, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H, 5″-H in unknown order), 7.67, 7.82 (m, 4 H, 2′-H, 6′-H, 2″-H, 6″-H in unknown order); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 14.85, 19.50 (d, C-4, C-5 in unknown order), 29.92 (t, C-7), 32.38 (d, C-6), 36.14 (d, C-3), 46.32, 48.94 (s, C-2, C-8 in unknown order), 87.45, 89.51 (s, C-1, C-9 in unknown order), 120.43, 120.63, (d, C-10a, C-11a in unknown order), 125.87, 126.15 (d, C-10b, C-11b in unknown order), 128.24, 128.35, 128.48 (d, C-2′, C-3′, C-5′, C-6′, C-2″, C-3″, C-5″, C-6″, in unknown order, 128.24 probably two signals), 128.48, 128.58 (d, C-4′, C-4″ in unknown order), 136.46 (s, C-1′, C-1″, this signal could be resolved to two singlets in D_6-DMSO), 148.24, 149.92 (s, C-10, C-11 in unknown order); MS (70 eV) *m/z* 360 (M^+, 14), 270 (10), 255 (100), 105 (35), 77 (11); HRMS calcd for $C_{27}H_{20}O$ 360.1514, found 360.1562. Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.15; H, 5.56.[31]

Generating and Trapping of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1-ene (4) with 1,2,3-Trimethylisoindole (9). **14** (200 mg, 1.58 mmol) in THF (2 mL) was added at 0 °C to a solution of LDA (1.90 mmol) and **9** (318 mg, 2.00 mmol) in anhydrous THF (10 mL). After being stirred for 20 h, the mixture was hydrolyzed with water (10 mL) and extracted with ether (2 × 10 mL). The organic layers were washed with water (10 mL), dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The crude dark red oil was dissolved in THF (20 mL) and added to a solution of maleic anhydride (196 mg, 2.00 mmol) and triethylamine (607 mg, 6.00 mmol) in ether/THF (1:1, 20 mL). After being stirred for 1 h, the solution was added to 2 N NaOH (20 mL) in a separating funnel and intensively shaken. The red solution was extracted with ether (3 × 20 mL), the organic layers were washed with water (2 × 20 mL), dried with $MgSO_4$, filtered, and the solvents were removed under reduced pressure. Evaporation at room temperature/4 × 10^{-4} Torr gave a red liquid which was distilled in a micro distillation apparatus. At 80 °C (bath)/4 × 10^{-4} Torr, about three drops of **19a** were obtained as a clear liquid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94, 1.79 (dd, ^2J = 10.8 Hz, ^3J = 1.6 Hz, NOE at δ 1.30, 2 H, 7-H_2), 1.30 (tt, ^3J = 1.2, 4.4 Hz, NOE at δ 1.54 and 1.57, 1 H, 6-H), 1.46 (s, NOE at δ 2.89 and 7.18, 3 H, C_9-CH_3), 1.54 (s NOE at δ 7.07, 3 H, C_1-CH_3), 1.54, 1.57 (m, 2 H, 4-H, 5-H in unknown order), 1.63 (s, 3 H, N-CH_3), 2.89 (d, ^3J = 2.0 Hz, 1 H, 3-H), 7.06, 7.18 (m, 2 H, 10a-H, 11a-H in unknown order), 7.08, 7.09 (m, 2 H, 10b-H, 11b-H in unknown order); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.48 (q, C_9-CH_3), 13.65 (q, C_1–CH_3), 14.41, 18.74 (d, C-4, C-5), 28.69 (q, NCH_3), 28.95 (t, C-7), 30.08 (d, C-6), 34.00 (d, C-3), 44.87, 48.24 (s, C-2, C-8 in unknown order), 68.42, 70.31 (s, C-1, C-9 in unknown order), 121.48, 121.84 (d, C-10a, C-11a in unknown order), 125.10, 125.44 (d, C-10b, C-11b in unknown order), 147.48, 149.47 (s, C-10, C-11); MS (70 eV) *m/z* 248 (M^+, 100), 234 (60), 219 (29), 178 (25), 159 (22); HRMS calcd for $C_{18}H_{19}N$ 248.114, found 248.161.

Isomerization of 18a. A suspension of **18a** (100 mg, 277 μmol) and di-μ-chlorobis(bicyclohepta-2,5-diene)dirhodium (**20**) (12.8

mg, 27.7 μmol) in carbon tetrachloride (5 mL) was stirred for 12 d. Ether (15 mL) was added, and the solution was subsequently washed with ethylenediamine tetraacetic acid disodium salt (EDTA, 3 × 10 mL) and water (2 × 10 mL). The organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue (58 mg, 58%) was analyzed by NMR spectroscopy. Warming to above room temperature led to the total polymerization of the product: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.53, 2.13 (dd, $^2J = 5.8$ Hz, $^3J = 1.5$ Hz, 2 H, 11-H_2), 3.73 (m, 1 H, 8-H), 6.25 (d, $^3J = 2.9$ Hz, 1 H, 7-H), 6.59 (d, $^3J = 5.2$ Hz, 1 H, 10-H), 6.90 (dd, $^3J = 5.3, 3.3$ Hz, 1 H, 9-H), 6.95, 7.40 (dm, $^3J_{ortho} = 7.0$ Hz, 2 H, 3a-H, 4a-H in unknown order), 7.11, 7.16 (td, $^3J_{ortho} = 7.2$ Hz, $^4J_{meta} = 1.1$ Hz, 2 H, 3b-H, 4b-H in unknown order), 7.37–7.48 (m, 6 H, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H, 5″-H in unknown order), 7.63, 7.72 (dm, $^3J_{ortho} = 7.2$ Hz, 4 H, 2′-H, 6′-H, 2″-H, 6″-H in unknown order); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 54.11 (d, C-8), 74.28 (t, C-11), 76.62 (s, C-1), 88.36, 89.35 (s, C-2, C-5 in unknown order), 118.92, 120.47, 140.29, 144.54 (d, C-3a, C-3b, C-4a, C-4b in unknown order), 126.14, 126.55, 127.26, 127.76, 128.58 (d, C-7, C-9, C-10, C-4′, C-4″ in unknown order), 126.65, 127.72, 128.40, 128.45 (d, C-2′, C-3′, C-5′, C-6′, C-2″, C-3″, C-5″, C-6″ in unknown order), 135.22, 137.56, 147.27, 148.38, 164.52 (s, C-6, C-3, C-4, C-1′, C-1″ in unknown order).

Computations. All the ab initio calculations were carried out using Gaussian 90[19] on a Cray Y-MP4/464.

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Supplementary Material Available: Tables of crystal data, X-ray experimental details, atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, selected torsional angles, and general displacement parameters and results of ab initio calculations containing geometrical parameters and energy values (18 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.