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SYNTHESIS, CHARACTERIZATION AND CRYSTAL DENSITY MODELING OF FOUR $C_{24}H_{28}$ CAGE-FUNCTIONALIZED ALKENES

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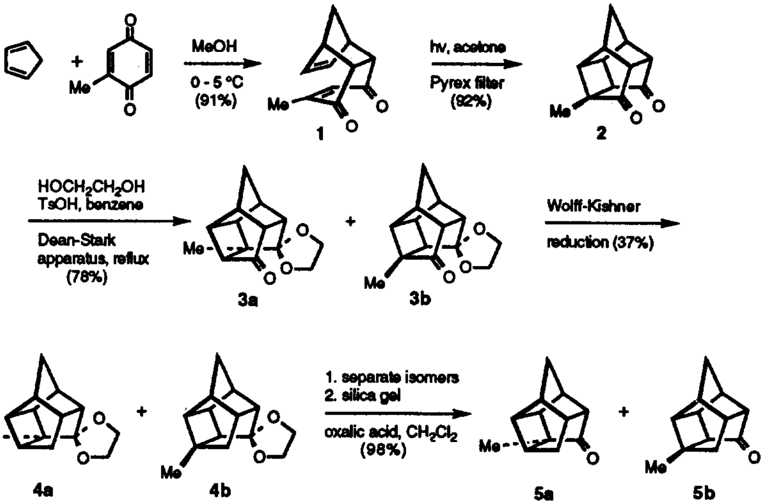
Abstract. Titanium-promoted reductive dimerization of methylated pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-ones, **5a**, **5b**, and **8**, afforded mixtures in each case of "methylated PCU alkene dimers" (**6a-d**, **7a-d**, and **9a**, respectively). Individual isomers have been isolated from these mixtures via column chromatography followed by multiple fractional recrystallization of individual chromatography fractions. Structures of four isomerically pure $C_{24}H_{28}$ alkenes, i.e., **6c**, **6d**, **7c**, and **9a** have been established unequivocally by application of single crystal X-ray crystallographic methods. The crystal density of each alkene (calculated from unit cell parameters) is compared with the results of theoretical density predictions.

Introduction. Polycarbocyclic "cage" compounds, by virtue of their compact structures, which often contain considerable amounts of strain energy, constitute an important class of high energy density materials.[1] Compounds of this type generally are highly dense (D_c = 1.2-1.3 g-cm^{-3}) and possess correspondingly high net volumetric heats of combustion, thereby rendering them of particular interest as high energy fuels for volume-limited applications.[2] As part of a continuing program which is concerned with the synthesis and chemistry of novel polycarbocyclic "cage" compounds,[3] we have employed the titanium-promoted reductive dimerization of cage ketones (McMurry reaction)[4] to synthesize several cage-functionalized C_{22}-C_{24} alkenes.[5]

We now report the results of a study of titanium-promoted reductive dimerization of 1- and of 7-methylpentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-one (**5a** and **5b**, respectively). Each of these reactions results in the formation of a mixture of $C_{24}H_{28}$ alkenes (**6** and **7**, respectively, Scheme 1) from which individual pure isomers have been isolated and fully characterized. In addition, insight into the factors which contribute to the unusually high density of these hydrocarbons has been gained via interpretation of the results of crystal density modeling calculations.

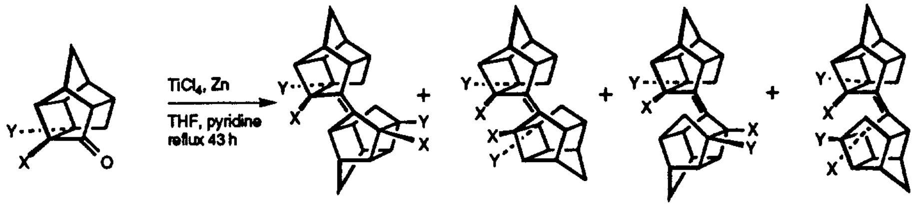
Synthesis of $C_{24}H_{28}$ Cage-Functionalized Alkenes. The method employed to synthesize **5a** and **5b** is outlined in Scheme 1. The mixture of mono(ethylene ketals) **3a** and **3b** produced by application of this procedure was not separated, but instead was used as obtained in the next synthetic step. Wolff-Kishner reduction[6] of the mixture of ketals afforded a mixture of **4a** and **4b**, which was separated by careful column chromatography on silica gel. Hydrolysis of each isomerically pure ketal, **4a** and **4b**, was performed by using a suspension of oxalic acid and silica gel in CH_2Cl_2,[7] thereby affording the corresponding ketones, **5a** and **5b**, respectively in excellent yield.

Scheme 1



Titanium promoted reductive dimerization of each isomerically pure ketone, **5a** and **5b**, was performed by using $TiCl_4$-Zn in the presence of pyridine.[8] Each of these reactions could afford mixtures of as many as four $C_{24}H_{28}$ alkenes (Scheme 2). In each case, isomerically pure alkenes could be isolated from the product mixture via careful column chromatography on $AgNO_3$ impregnated silica gel by using hexane as eluent, followed by fractional recrystallization of individual chromatography fractions from pentane or hexane. In this manner, three isomerically pure alkenes, **6c** (mp 186-187 °C), **6d** (mp 185-186 °C), and **7c** (mp 181-182 °C) were isolated.

Scheme 2

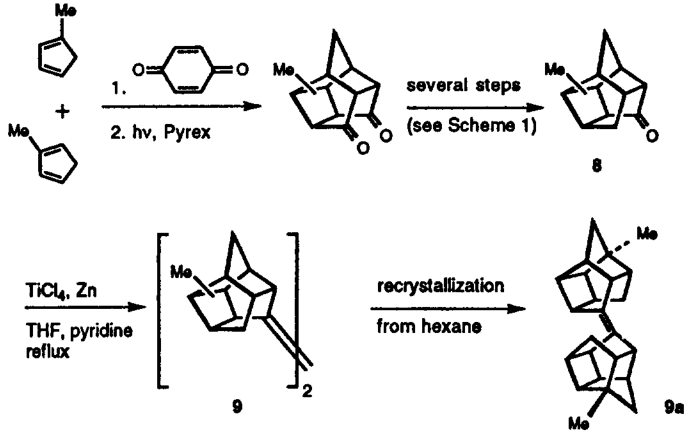


5a: X = Me, Y = H
5b: X = H, Y = Me

6a: X = Me, Y = H **6b**: X = Me, Y = H **6c**: X = Me, Y = H **6d**: X = Me, Y = H
7a: X = H, Y = Me **7b**: X = H, Y = Me **7c**: X = H, Y = Me **7d**: X = H, Y = Me

In addition, a fourth $C_{24}H_{28}$ alkene, **9a**, was prepared via a synthetic route which is closely related to that shown in Scheme 1, the primary difference being that the reaction sequence was initiated via Diels-Alder reaction of a mixture of 1- and 2-methylcyclopentadienes with *p*-benzoquinone (see Scheme 3).[9] Titanium-promoted reductive dimerization of the mixture of methylated pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-ones, **8**, thereby obtained afforded a gross mixture of the corresponding methylated alkene dimers, **9**. Interestingly, a single pure isomer, **9a**, mp 256-257 °C, could be obtained readily via recrystallization of the crude product from hexane. The structures of the four $C_{24}H_{28}$ alkenes which were prepared in this study (i.e., **6c**, **6d**, **7c**, and **9a**) were established unequivocally via single crystal X-ray structural analysis (see the Experimental Section and Table 1).

Scheme 3



Results of Crystal Density Calculations. The prediction of the crystal density of an unknown compound typically has been approached through the use of "volume additivity" procedures.[10] Here, the crystal-molecular volume (V_{cm}) is calculated by summing appropriate crystal-atomic or group volumes (V_{ca}; $V_{cm} = \Sigma V_{ca}$) and the corresponding crystal density is obtained by dividing the molecular mass (M) by V_{cm}; thus, $\rho = M/V_{cm}$. V_{ca} values usually are obtained by least-squares procedures which fit V_{cm} values to experimental crystal-molecular volumes (V_{ce}) from X-ray crystal structure data (V_{ce} = unit cell volume divided by the number of molecules per unit cell).

It should be noted that the molecular volume (V_m), calculated from a molecule's three-dimensional structure and appropriate atomic van der Waals radii, is smaller than V_{cm} because only a fraction (typically 0.55 - 0.80) of the unit cell volume is filled with molecules. The term "packing efficiency", $PC = V_m/V_{ce}$, has been used to express the "occupied" fraction of the unit cell volume. Because the derivation of V_{ca} values involves crystals that possess a range of packing efficiencies, some "average PC" is built into the additivity volumes.[11]

Volume additivity methods generally do not take into account crystal packing efficiency or molecular conformation effects and thus will afford identical calculated densities for positional and conformational isomers and for compounds that possess different multiples of the same functional group composition. As an example, a volume additivity calculation predicts that 1,3,5-trinitro-1,3,5-triazacyclohexane [RDX, $(CH_2NNO_2)_3$], 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane [α-HMX, $(CH_2NNO_2)_4$], and β-HMX all will possess the same crystal density, 1.783 g-cm^{-3}.[10e] In fact, the experimentally observed densities of these three compounds differ markedly (i.e., 1.806[12] 1.839,[13] and 1.902,[14] respectively).

Recently, Holden, Du, and Ammon[15] reported a procedure for predicting possible crystal structures of C, H, N, O, and F-containing organic compounds. Their approach involves construction of crude crystal packing arrangements (MOLPAK = MOLecular PacKing program), starting with an optimized model (search probe) for the compound of interest, by positioning molecules around a central molecule into predetermined coordination sphere geometries. The best of these arrangements are refined subsequently with a crystal lattice energy minimization (WMIN[16]) program. This procedure takes molecular shape, conformation, and crystal packing efficiency into account. It was of interest to test the applicability of the MOLPAK/WMIN procedure as a method for predicting the crystal densities of the four isomeric $C_{24}H_{28}$ alkenes, **6c**, **6d**, **7c**, and **9a**, whose X-ray crystal structures (and corresponding crystal densities) are reported herein.

The current version of MOLPAK contains molecular coordination geometry routines for the triclinic, monoclinic, and orthorhombic space groups with one molecule per asymmetric unit. At present, there is no provision for handling molecules that utilize crystallographic symmetry (e.g., an inversion center or two-fold rotation axis). Of the four alkenes of interest, **6c**, **7c**, and **9a** possess inversion symmetry, while **6d** straddles a crystallographic two-fold symmetry axis. Although our predictions thus are limited to crystal densities, the calculations of Holden *et al.*[15] indicate that many compounds possess several minimum energy hypothetical structures with virtually identical densities.

Preliminary models for the alkenes of interest were constructed with either Chem3D Plus™[17] (Macintosh IIci, University of North Texas) or QUANTA[18] (IBM RS/6000, model 370, University of Maryland). Geometry optimizations were performed by using the AM1 procedure in MOPAC[19] on the IBM RS/6000. The AM1 derived geometries were modified to set all C-H bond lengths to 1.098 Å, a value that was used for all compounds when developing the energy coefficients in the WMIN force field. MOLPAK/WMIN calculations of crystal structure and density predictions were performed on a number of platforms, e.g., RS/6000, DEC VaxStation 3100, DecStation 5000, model 240, and a DEC Alpha AXP 3000, model 400. The calculations covered six space group/coordination environments (i.e., two in P1, two in $P2_1/c$, and one in each $P2_1$ and $P2_12_12_1$).

The observed (experimental) crystal densities and space groups, the corresponding densities obtained from a WMIN refinement of the observed crystal structures, and the corresponding densities and space groups predicted by the results of MOLPAK/WMIN calculations are presented in order of increasing observed crystal density in Table 1. Compounds **7c** and **9** provide the density extremes, with those of **6c** and **6d** at similar intermediate values. This trend is repeated by the densities obtained from WMIN-refined observed crystal structures, but in this case there is relatively little difference among the densities of **6c**, **6d**, and **9a**. The predicted densities are close to the corresponding observed and WMIN-refined values. Here, the densities of **6c**, **6d**, and **9a** are essentially identical. Of interest is the fact that **7c** displays the lowest density value in all three sets.

It should be emphasized that the value of 1.255 g cm^{-3} predicted for **6d** was obtained by using a crystal structure model as the search probe in the MOLPAK procedure. The use of an AM1 model for the search probe gave a maximum density of 1.199 g cm^{-3}, a value which is 4.9% smaller than observed. A Chem3D™ comparison of the X-ray and AM1-derived structures for **6d** is shown in Figure 1. The rms deviation of the 24 carbon atoms in the two structures is 0.31 Å. The seemingly small differences that become apparent upon close inspection of the structure drawings in Figure 1 nevertheless appear to be sufficient to prevent efficient packing of the AM1-derived structure. In a future study, we plan to optimize the **6d** model geometry by using an extended basis set calculation in Gaussian 92.

Table 1. Comparison of observed and predicted densities (g-cm^{-3}) for **6c**, **6d**, **7c**, and **9a**

Compound	ρ_{obsd}	ρ_{WMIN} $(\Delta)^a$	ρ_{pred} $(\Delta)^a$	space group^c
7c	1.212	1.232 (+ 1.43%)	1.220 (+ 0.66%)	$P2_1$ and $P\bar{1}$
6c	1.251	1.259 (+ 0.67%)	1.254 (+ 0.24%)	$P2_1/c$
6d	1.261	1.255 (- 0.47%)	1.255 (- 0.47%)^b	$P2_12_12_1$
9a	1.286	1.263 (- 1.81%)	1.255 (- 2.40%)	$P\bar{1}$

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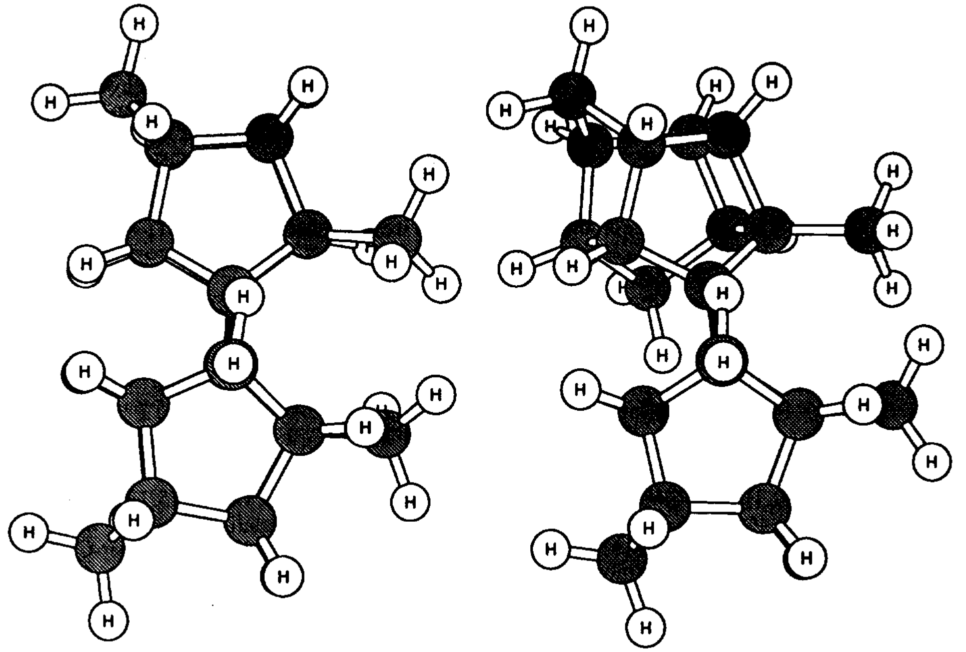
[a] $\Delta = 100\ (\rho_{calcd} - \rho_{obsd})/(\rho_{obsd})$.

[b] Predicted density obtained with an X-ray structure model as the MOLPAK search probe. Use of an AM1 search probe instead afforded $\rho_{pred} = 1.199$ g cm^{-3} (- 4.92%).

[c] The MOLPAK space group (coordination symmetry) which afforded the largest density value.

The molecular volumes (V_m's) calculated for the X-ray models of **7c**, **6c**, **6d** and **9a** are 284.6, 284.9, 284.5 and 286.2 Å^3, respectively. Given the relationship between crystal density, packing coefficent and molecular density ($\rho_m = M/V_m$; $\rho = PC \times \rho_m$), it is interesting to note that the molecule which possesses the lowest molecular density has the highest crystal density. This underscores the efficient crystal packing that exists in **9a** *vis-à-vis* the other three compounds.



AM1 model X-ray model

Figure 1. A comparison of the AM1 and X-ray models for **6d** drawn with Chem3D™.

Experimental Section

Melting points are uncorrected.

1-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione Mono(ethylene ketal) (3a and 3b)[20]. Into a 100 mL round-bottom flask which had been fitted with a reflux condenser and a Dean-Stark apparatus were placed 1-methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione[21] (**2**, 321 mg, 1.67 mmol), ethylene glycol (121 mg, 1.83 mmol), TsOH (30 mg, catalytic amount), and benzene (50 mL). The resulting mixture refluxed, and water was removed by azeotropic distillation during 5 h. The resulting mixture was allowed to cool to room temperature and then was washed successively with 5% aqueous $NaHCO_3$ (3 x 10 mL), water (1 x 10 mL), and brine (1 x 10 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a brown oil, was purified via column chromatography on silica gel by using 20% EtOAc-hexane as eluent. A mixture of **3a** and **3b** (301 mg, 78%) was thereby obtained as a brown oil; IR (neat) 2971 (s), 2950 (s), 2880 (m), 2859 (m), 1738(s), 1442 (w), 1337 (m), 1316 (m), 1217 (m), 1097 (m), 1027 (m), 942 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.03 (d, J = 1.5 Hz, 6 H), 1.46 (AB, J_{AB} = 11.4 Hz, 2 H), 1.74 (AB, J_{AB} = 11.0 Hz, 2 H), 2.05-2.16 (m, 2 H), 2.21-2.56 (m, 8 H), 2.52-2.90 (m, 4 H), 3.67-3.88 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 15.88 (q), 16.43 (q), 33.55 (d), 38.64 (d), 38.96 (t), 39.11 (t), 41.94 (d), 42.55 (d), 42.58 (d), 42.66 (d), 44.36 (s), 44.81 (s), 45.44 (d), 46.97 (d), 47.90 (d), 48.67 (d), 50.76 (d), 50.91 (d), 52.61 (d), 53.50 (d), 64.30 (t), 65.22 (t), 65.49 (t), 66.11 (t), 114.1 (s), 114.2 (s), 214.4 (s), 214.9 (s). This material was used as obtained without further purification or characterization.

Wolff-Kishner Reduction of a Mixture of 3a and 3b. To a 100 mL round bottom flask fitted with a reflux condenser were added under argon a solution which contained a mixture of **3a** and **3b** (1.00 g, 4.31 mmol) in diethylene glycol (30 mL), K_2CO_3 (5.95 g, 43.1 mmol) and anhydrous hydrazine (1.38 g, 43.1 mmol). The reaction mixture was heated with stirring under argon at 160 °C for 4 h. The reaction vessel then was fitted with a Dean-Stark apparatus, and water was removed from the reaction mixture by azeotropic distillation. The temperature of the reaction mixture rose gradually as the distillation continued until it reached 220 °C. The reaction temperature was maintained continuously at 220 °C for 5 h. and then was allowed to cool to room temperature. Water (100 mL) was added, and the resulting suspension was extracted with Et_2O (3 x 25 mL). The combined ether layers were washed with water (1 x 20 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo*, thereby affording a brown oil (838 mg, 89%). The crude product was purified via column chromatography on silica gel by using 20% EtOAc-hexane as eluent. A mixture of 1-methyl- and 7-methyl-8-[2'-(1',3'-dioxolano)]pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**4a** and **4b**), was thereby obtained as a yellow oil (353 mg, 37%). This material was further purified via column chromatography on silica gel (pentane eluent). The first chromatography fraction was concentrated *in vacuo*, thereby affording pure **4a** as a colorless oil (120 mg, 12%); IR (neat) 2970 (br, s), 2857 (s), 1449 (s), 1179 (m), 1080 (s), 1017 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.05 [t(AB), J_{AB} = 11.8 Hz, J = 4.0 Hz, 1 H]; 1.21 (*A*B, J_{AB} = 10.6 Hz, 1 H), 1.62 (A*B*, J_{AB} = 10.3 Hz, 1 H), 1.95-2.14 (m, 3 H), 2.22-2.40 (m, 4 H), 2.51 (br q, J = 6.0 Hz, 1 H), 3.68-4.03 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.69 (q), 29.31 (d), 35.69 (t), 36.65 (d), 42.96 (d), 43.21 (d), 43.37 (d), 45.37 (d), 45.60 (s), 47.23 (d), 48.21 (d), 63.46 (t), 66.04 (t), 117.2 (d).; mass spectrum, *m/e* (relative intensity) 218 (parent ion, 100), 153 (31.8), 109 (24.4), 99 (11.5), 91 (19.7), 79 (10.8), 66 (11.7); Anal. Calcd for $C_{14}H_{18}O_2$: Calcd M_r 218.1307. Found (high-resolution mass spectrometry): M_r 218.1303.

Continued elution of the chromatography column afforded a second fraction which was concentrated *in vacuo*, thereby affording pure **4b** as a colorless oil: IR (neat) 2935 (br, s), 2862 (m), 1340 (m), 1314 (m), 1120 (m), 1109 (m), 1024 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.91 [d(AB), J_{AB} = 11.5 Hz, J = 2.9 Hz, 1 H], 1.09-1.27 (m, 4 H), 1.60 (AB, J_{AB} = 10.2 Hz, 1 H), 1.78-2.16 (m, 4 H), 2.24-2.50 (m, 4 H), 3.63-3.96 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.92 (q), 35.71 (d), 35.88 (t), 36.57 (d), 43.32 (d), 43.34 (s), 44.10 (d), 46.72 (d), 46.78 (d), 47.72 (d), 48.00 (d), 62.49 (t), 65.33 (t), 117.5 (s); mass spectrum, *m/e* (relative intensity) 218 (parent ion, 100), 203 (5.6.0), 139 (72.9), 126 (61.2), 95 (53.8), 77 (27.9); Anal. Calcd for $C_{14}H_{18}O_2$: Calcd M_r 218.1307 Found (high-resolution mass spectrometry): M_r 218.1313.

7-Methylpentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one (5a).[7] To a suspension of silica gel (9.0 g) in CH_2Cl_2 (60 mL) was added a saturated aqueous solution of oxalic acid (0.9 mL, 1.1 mmol), and the resulting mixture was stirred for 10 minutes. Compound **4a** (92 mg, 0.42 mmol) then was added, and the resulting mixture was stirred at room temperature for 25 h. Solid $NaHCO_3$ then was added, and the resulting mixture was stirred at room temperature for 15 minutes. The reaction mixture was filtered, and the filtrate was washed with CH_2Cl_2 (5 x 25 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. Pure **5a** (72 mg, 98%) was thereby obtained as a yellow oil; IR (neat) 2956 (br, s), 2864 (m), 1734 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.21 (s, 1 H), 1.33-1.41 (m, 2 H), 1.50 (*A*B, J_{AB} = 10.2 Hz, 1 H), 1.84 (A*B*, J_{AB} = 10.2 Hz, 1 H) 2.14 (br s, 1 H) 2.26-2.54 (m, 3 H), 2.64-2.93 (m, 1 H), 2.87 (q, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.41 (q), 31.23 (t), 38.05 (t), 40.77 (d), 42.08 (d), 43.05 (d), 46.52 (d), 47.36 (s), 47.82 (d), 48.27 (d), 53.29 (d), 221.7 (s).

Compound **5a** was further characterized via the corresponding 2,4-dinitrophenylhydrazone. Thus, to a solution of 2,4-dinitrophenylhydrazine (90 mg, 0.46 mmol) in EtOH (20 mL) were added **5a** (100 mg, 0.46 mmol) and concentrated H_2SO_4 (one drop), and the resulting mixture was stirred at room temperature for 15 minutes. The reaction mixture then was cooled by application of an external ice-water bath, whereupon an orange precipitate formed. This material was collected by suction filtration, and the residue was washed with cold EtOH (5 mL). Recrystallization of the crude product thereby obtained from $CHCl_3$ afforded the 2,4-dinitrophenylhydrazone derivative of **5a** (170 mg, 95%) as an orange microcrystalline solid: mp 193-194°C; IR (KBr) 3949 (br, s), 2972 (s), 1610 (s), 1581 (s), 1445 (s), 1410 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.20-1.50 (m, 6 H), 1.89 (d, J = 10.9 Hz, 1 H), 2.34-2.44 (m, 1 H), 2.46-2.59 (m, 3 H), 2.67-2.82 (m, 2 H), 3.16 (ddd, J = 9.8, 4.3, 1.4 Hz, 1 H), 7.91 (d, J = 9.6 Hz, 1 H), 8.24 (ddd, J = 9.5, 2.6, 0.7 Hz, 1 H), 9.09 (d, J = 2.6 Hz, 1 H), 11.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.27 (q), 31.23 (t), 37.15 (t), 40.07 (d), 43.82 (d), 45.49 (d), 46.03 (d), 46.09 (d), 46.42 (s), 47.03 (d), 47.08 (d), 116.2 (d), 123.7 (d), 128.5 (s), 129.8 (d), 137.2 (s), 145.6 (s), 171.7 (s). Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 60.85; H, 5.39.

1-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (5b).[7] The same procedure that was used to hydrolyze **4a** (*vide supra*) was used for the corresponding hydrolysis of **4b** (92 mg, 0.42 mmol). Workup of the reaction afforded **5b** as a pale yellow oil (72 mg, 98%); IR (neat) 2951 (br, m), 2816 (m), 1733 cm^{-1} (br, s); ^{1}H NMR ($CDCl_3$) δ 1.17-1.32 (m, 4 H), 1.46 (*A*B, J_{AB} = 10.8 Hz, 1 H), 1.78 (A*B*, J_{AB} = 10.6 Hz, 1 H), 2.05-2.27 (m, 2 H), 2.37-2.76 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 23.51 (q), 33.92 (d), 37.80 (t), 38.15 (t), 43.03 (d), 48.00 (s), 48.17 (d), 48.32 (d), 49.54 (d), 51.00 (d), 51.70 (d), 221.0 (s).

Compound **5b** was further characterized via the corresponding 2,4-dinitrophenylhydrazone by using the same procedure that had been employed previously for the corresponding synthesis of the 2,4-dinitrophenylhydrazone derivative of **5a** (*vide supra*). Pure **5b** was thereby obtained as an orange microcrystalline solid: mp 169-170 °C; IR (KBr) 3218 (s), 2952 (m), 2816 (m), 1733 cm^{-1} (br, s); ^{1}H NMR ($CDCl_3$) δ 1.11-1.68 (m, 6 H), 1.82 (d, *J* = 12.6 Hz, 1 H), 2.32-2.85 (m, 6 H), 2.93-3.07 (m, 1 H), 7.91 (d, *J* = 9.5 Hz, 1 H), 8.18-8.32 (m, 1 H), 9.10 (d, *J* = 2.6 Hz, 1 H), 10.98 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.74 (q), 36.08 (t) 37.39 (d), 37.30 (t), 42.39 (d), 44.36 (d), 47.98 (d), 48.01 (d), 48.11 (d), 48.24 (s), 48.28 (d), 116.1 (d), 123.7 (d), 129.5 (s), 129.9 (d), 137.3 (s), 145.2 (s), 171.2 (s); Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 60.85; H, 5.17.

Titanium Promoted Reductive Dimerization of 5a.[8] Dry THF (25 mL) was placed in a 50 mL round-bottom flask which had been fitted with a reflux condenser. The system was flushed with argon and then cooled externally to -78 °C by application of a dry ice-acetone bath. Titanium tetrachloride (2.0 mL, 15 mmol) was added dropwise (via syringe) with stirring to the cooled reaction flask. Stirring was continued for 15 minutes after all of the $TiCl_4$ had been added, at which time Zn dust (2.74 g, 30.8 g-atom) was added portionwise with stirring. After addition of the Zn had been completed, the reaction mixture was refluxed for 1 h and then allowed to cool gradually to room temperature. Pyridine (0.5 mL) and **5a** (1.50 g, 7.73 mmol) then were added, and the resulting mixture was refluxed for 24 h. The reaction mixture was allowed to cool to room temperature, and the reaction then was quenched via addition of 10% aqueous HCl (20 mL). The resulting mixture was stirred for 30 minutes and then was extracted with Et_2O (3 x 30 mL). The combined ether extracts were washed with water (20 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo*, thereby affording a mixture of alkene dimers, **6a-6d** (851 mg, 62%). This material was purified via careful column chromatography on silica gel by using hexane as eluent. Separation of individual isomers from the product thereby obtained (758 mg) was accomplished via column chromatography on $AgNO_3$ impregnated silica gel (400 mesh). The first chromatography fraction afforded isomerically pure **6c** as a colorless microcrystalline solid: mp 186-187°C; IR (KBr) 2970 (m), 2946 (s), 2921 (s), 2915 (s), 2853 (m), 1596 (w), 1435 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.05 [t(AB), *J* = 3.3, 10.2 Hz, 1 H], 1.22 (m, 2 H), 1.39 (s, 3 H), 1.59 (A*B*, J_{AB} = 10.0 Hz, 1 H), 1.99-2.27 (m, 5 H), 2.42-2.59 (m, 1 H), 3.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.61 (q), 30.26 (t), 35.55 (t), 39.83 (d), 44.44 (d), 44.80 (d), 46.39 (d), 46.58 (d), 47.89 (s), 49.08 (d) 51.00 (d), 135.2 (s). Anal. Calcd for $C_{24}H_{28}$: C, 91.03; H, 8.92. Found: C, 90.89; H, 8.86. The structure of **6c** was established unequivocally by X-ray crystallographic methods (*vide infra*).

The second chromatography fraction afforded **6d** as a colorless microcrystalline solid: mp 185-186° C; IR (KBr) 2958 (m), 2946 (s), 2921 (s), 2890 (s), 2854 (m), 1596 (w), 1448 (w), 1429 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.07 [t(AB), *J* = 12.0, 3.0 Hz, 1 H], 1.24 (m, 2 H), 1.36 (s, 3 H), 1.58 (*A*B, J_{AB} = 10.1 Hz, 1 H), 2.09-2.32 (m, 5 H), 2.45-2.62 (m, 1 H), 2.95 (dt, *J* = 9.6, 3.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.96 (q), 30.60 (t), 35.19 (t), 39.78 (d), 42.95 (d), 44.80 (d), 45.37 (s), 46.08 (d), 46.25 (d), 51.97 (d), 54.33 (d), 136.6 (s). Anal. Calcd for $C_{24}H_{28}$: C, 91.03; H, 8.92. Found: C, 91.01; H, 8.80. The structure of **6d** was established unequivocally by X-ray crystallographic methods (*vide infra*).

Titanium Promoted Reductive Dimerization of 5b.[8] The same procedure that was used to dimerize **5a** was used again to promote the corresponding reductive dimerization of **5b** (900 mg, 4.64 mmol, *vide supra*). Workup of the reaction mixture thereby obtained afforded the corresponding alkene dimer as a mixture of isomers (**7a-7d**, 594 mg, 64%). This material was purified via careful column chromatography on silica gel (hexane eluent). A mixture of isomeric dimers (467 mg, 50%) was obtained via column chromatography by using hexane as eluent. Multiple recrystallizations from pentane afforded isomerically pure **7c** as a colorless microcrystalline solid: mp 181-182 °C; IR (KBr) 2921 (s), 2847 (s), 1546 (w), 1516 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 0.83 [d(*A*B), *J* = 11.5 Hz, 3.2 Hz, 1 H], 1.02 (A*B*, J_{AB} = 11.5, 1 H), 1.14 (s, 3 H), 1.22 (*A*B, J_{AB} = 11.0 Hz, 1 H), 1.58 (A*B*, J_{AB} = 11.0, 1 H), 2.02-2.36 (m, 4 H), 2.45-2.63 (m, 3 H); ^{13}C NMR (C_6D_6) δ 23.82 (q), 29.17 (d), 36.04 (t), 37.24 (t), 40.29 (d), 45.60 (d), 46.01 (d), 46.10 (s), 46.89 (d), 47.88 (d), 48.98 (d), 134.0 (s). Anal. Calcd for $C_{24}H_{28}$: C, 91.03 H, 8.92. Found: C, 91.10; H, 8.76. The structure of **7c** was established unequivocally by X-ray crystallographic methods (*vide infra*).

Titantium-Promoted Reductive Dimerization of 8.[9] The procedure which was employed for titanium-promoted reductive dimerization of **8** (12.18 g, 70 mmol) is essentially the same as that which was used previously for the corresponding reductive dimerizations of **5a** and **5b** (*vide supra*) and has been described in detail elsewhere.[9] The crude reaction product was purified via column chromatography on silica gel (hexane eluent). The purified product, a gross mixture of several isomeric $C_{24}H_{28}$ alkenes, **9** (8.0 g, 73%), was thereby obtained as a colorless microcrystalline solid that melted over a wide range (mp 95-110 °C). Fractional recrystallization of this material from hexane afforded pure **9a** as colorless rhombic crystals: mp 256-257 °C; IR (KBr) 2965 (s), 2954 (m), 2930 (s), 2856 (m), 1430 cm^{-1} (w); ^{1}H NMR (CDCl$_3$) δ 1.01 (s, 6 H), 1.08-1.34 (m, 6 H), 1.40-1.60 (m, 2 H), 1.78-1.92 (m, 2 H), 1.94-2.28 (m, 4 H), 2.44-2.78 (m, 6 H), 2.89 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 19.09, 27.36, 28.94 , 38.84, 39.31, 42.67, 44.71, 46.21, 47.90, 48.35, 50.11, 53.38, 133.6. Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.02; H, 9.01. The structure of **9a** was established unequivocally by X-ray crystallographic methods (*vide infra*).

X-ray Structure Determinations of 6c, 6d, 7c, and 9a. All data were collected on an Enraf-Nonius CAD-4 diffractometer with the θ -2θ scan technique, Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard X-ray crystallographic procedures which have been used in our laboratory have been described previously.[22] Pertinent X-ray data are given in Table 2. Data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods (MULTAN)[23]; in each case, the model was refined by using full-matrix least squares techniques. The treatment of the thermal parameters was based upon connectivity. Hydrogen atoms were located on difference maps and then included in the model in idealized positions [U(H) = 1.3B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[24] Scattering factors were taken from the usual sources.[25]

Table 2. X-ray structure data for **6c**, **6d**, **7c**, and **9a**.[26]

Compound	**6c**	**6d**	**7c**	**9a**
Formula	$C_{24}H_{28}$	$C_{24}H_{28}$	$C_{24}H_{28}$	$C_{24}H_{28}$
Size (mm)	0.2 x 0.2 x 0.3	.08 x .22 x .42	.07 x .22 x .41	.11 x .46 x .52
Space Group	$P2_1/n$	$P2_12_12$	$P2_1/n$	P1
a (Å)	9.8445 (8)	10.754 (2)	7.330 (1)	6.150 (5)
b (Å)	7.4692 (5)	10.031 (2)	12.113 (1)	6.446 (4)
c (Å)	12..2101 (6)	7.724 (3)	9.778 (2)	11.598 (5)
a (°)	90	90	90	78.74 (4)
b (°)	110.647 (5)	90	92.86 (2)	85.87 (5)
g (°)	90	90	90	64.95 (5)
V (Å^3)	840.1 (1)	833.2 (4)	867.1 (4)	408.5
Z	2	2	2	1
D_c (g-cm^{-3})	1.251	1.261	1.212	1.286
m (cm^{-1})	0.65	0.66	0.63	0.67
$2q_{max}$	44	44	44	46
Total refl.	1185	2366	1224	1135
Unique refl.	1121	633	1131	1135
R_{int}	0.025	0.032	0.032	- -
I ≥ 3s(I)	777	329	513	957
Parameters	109	64	84	109
R, wR	0.0550, 0.0561	0.0537, 0.0551	0.0658, 0.0683	0.0362, 0.0518
$(D/s)_{max}$	<0.01	<0.01	<0.01	<0.01
$r_{min}; r_{max}$	0.311, -0.245	0.170, -0.211	0.223, -0.261	0.172, -0.168

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