evident by the loss of the bis(trimethylsilyl)amine methyl signal (2.6 ppm) and the formation of LBTSA methyl signals (5.7 and 6.4 ppm). Warming the sample to room temperature resulted in coalescence of the methyl resonances at 6.0 ppm. It is known that a monomer–dimer equilibrium of LBTSA exists in THF.[8] Presumably, at −73 °C, the exchange rate between the monomer and dimer is slow on the NMR time scale, and the nonaveraged, different environments of the two species result in two signals being observed for the methyl groups. At room temperature the exchange rate is rapid so that only one averaged signal is observed for the methyl groups.[9]

The final example studied was the synthesis of lithium 2,2,6,6-tetramethylpiperidide. The spectral data for the reaction of 2,2,6,6-tetramethylpiperidine with the *n*-butyllithium hexanes solution at −73 °C revealed that the reaction was complete within 2 min. This result was concluded from the loss of the 2,2,6,6-tetramethylpiperidine α-carbon signal (49.8 ppm) and the formation of the LTMP α-carbon signal (52.7 ppm). When the reaction was warmed to room temperature, a change in peak shape was observed for several of the peaks. However, when the solution was cooled again to −73 °C, the spectrum was identical with the low-temperature spectrum taken within the first 2 min. The change in peak shape may be attributed to an equilibrium between complexing species of LTMP.[9]

Several different lithium reagents were also examined. The reaction of 2,2,6,6-tetramethylpiperidine with a methyllithium ether solution in the THF/TMS solvent system was investigated at −73 °C. LTMP was formed to a major extent, although not completely, after 15 min at −73 °C. When the sample was warmed to 0 °C, the spectrum, taken within 5 min, revealed complete formation of LTMP. This result indicates that room temperature conditions are not required to rapidly form LTMP from the reaction of methyllithium with 2,2,6,6-tetramethylpiperidine.

Phenyllithium in ether/cyclohexane was examined in the THF/TMS solvent system with 2,2,6,6-tetramethylpiperidine at −73 °C. After 10 min essentially no reaction had occurred. The sample was warmed to 0 °C and after 10 min only a slight increase in LTMP was observed. Therefore, the reaction was warmed to room temperature. A slight increase in LTMP was indicated after 15 min; however, the majority of 2,2,6,6-tetramethylpiperidine was left unreacted.

The difference in the rate of LTMP formation, depending on the lithium reagent used, is believed to be due to the difference in base strength of the particular lithium reagent.[2] The most basic lithium reagent, *n*-butyllithium, generated LTMP rapidly at −73 °C while the least basic reagent, phenyllithium, was slow even at room temperature. Methyllithium, being intermediate in base strength, required an intermediate temperature, 0 °C, for rapid complete formation of LTMP.

In conclusion, we have confirmed the low-temperature formation of several lithium amide bases. LDA, LBTSA, or LTMP was quantitatively generated at −73 °C in THF within 2 min of mixing *n*-butyllithium with diisopropylamine, bis(trimethylsilyl)amine, or 2,2,6,6-tetramethylpiperidine, respectively. The fact that LDA, LBTSA, and LTMP are rapidly formed at low temperature indicates that current experimental manipulations can be simplified and that the time required to conduct a procedure utilizing one of these lithium amide bases can be shortened. This method should be applicable in determining the effect reaction conditions have on the formation of other lithium amide bases and may prove especially useful when examining hindered lithium amide base formation.[10]

Experimental Section

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian XL-400 spectrometer. Tetrahydrofuran was used as the solvent, with tetramethylsilane as the internal reference. Spectrometer shimming was optimized with THF-d_8/TMS at −73 °C prior to running the actual reaction samples. The chemical shift assignments were referenced to internal tetramethylsilane. The lithium reagents were purchased from Aldrich and were titrated before use. Tetrahydrofuran was distilled from lithium aluminum hydride, and diisopropylamine, bis(trimethylsilyl)amine, and 2,2,6,6-tetramethylpiperidine were distilled from calcium hydride under nitrogen.

Evaluation of LDA Formation. Typical Procedure. A standard 5-mm NMR tube containing 0.07 mL (0.5 mmol) of diisopropylamine in 0.5 mL of THF was chilled to −73 °C in the NMR probe.[11] A ^{13}C NMR spectrum was recorded.[12] By syringe, 0.22 mL of *n*-butyllithium (2.3 M *n*-butyllithium in hexanes, 0.5 mmol) was rapidly added to the chilled solution. The tube was then shaken and reinserted in the NMR probe, all within approximately 30 s. The ^{13}C NMR spectrum was acquired within 2 min of addition of the lithium reagent, followed by additional data collection at 5-, 10-, and 15-min intervals. After the 15-min measurement, the NMR tube was removed from the probe and allowed to warm to room temperature, and the room temperature ^{13}C NMR spectrum was recorded.

Acknowledgment. We thank Drs. Richard Cox, Jeff Seeman, Rett Southwick, and Jan Wooten for stimulating comments.

Registry No. LDA, 4111-54-0; LBTSA, 4039-32-1; LBTSA (dimer), 97587-69-4; LTMP, 38227-87-1; diisopropylamine, 108-18-9; bis(trimethylsilyl)amine, 999-97-3; 2,2,6,6-tetramethylpiperidine, 768-66-1.

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(11) No special atmospheric precaution is necessary since identical results were obtained with nitrogen and air atmospheres.
(12) The ^{13}C NMR spectrum was recorded to allow assignment of the chemical shifts of the amine.

Transannular Cyclizations in the Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione System: A Reinvestigation

Alan P. Marchand,* Benny E. Arney, Jr., Paritosh R. Dave, and N. Satyanarayana

Department of Chemistry, University of North Texas, Box 5068, Denton, Texas 76203

William H. Watson* and Ante Nagl

Department of Chemistry, Texas Christian University, Box 32908, Fort Worth, Texas 76129

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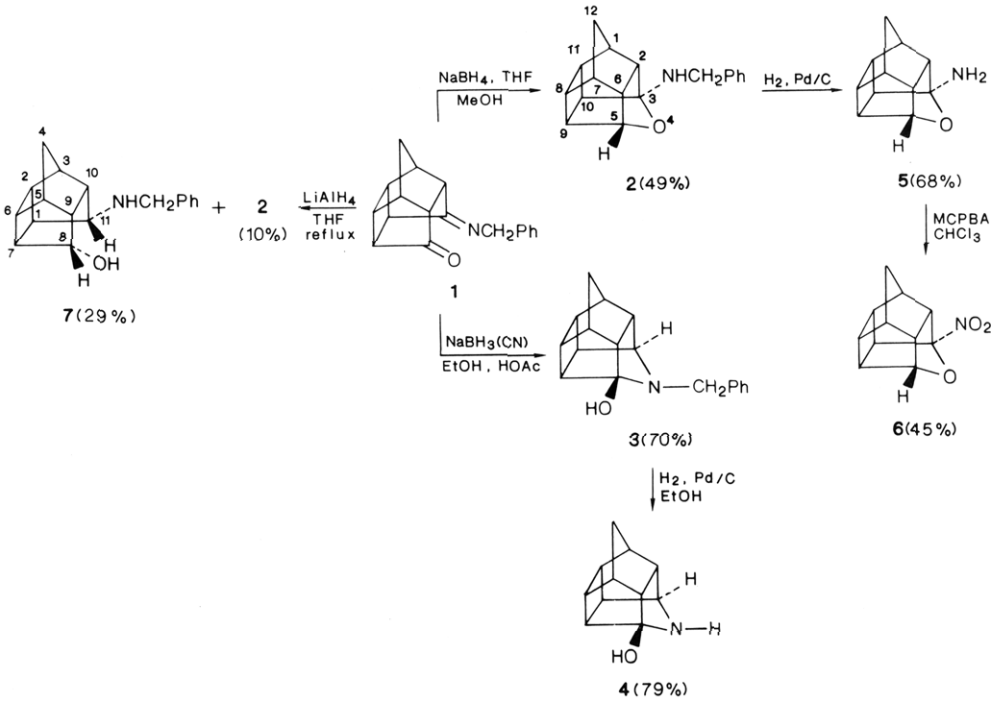
As part of an ongoing program that is involved with the synthesis and chemistry of polycyclic "cage" compounds,[1] we have examined some interesting imine and ketone reductions in the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane ring

(1) See: Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT; Vol. 1, in press and references cited therein.

0022-3263/88/1953-2644$01.50/0

Scheme I



system. These reductions result in the formation of heterocyclic hexacyclic cage systems via transannular cyclization reactions. Some of these reactions were studied previously by Sasaki and co-workers.[2] As work progressed, we became aware of some discrepancies in spectral properties between compounds that we prepared and those that had been reported earlier.[2] This led us to reexamine their earlier work in the light of our current findings. We now report the results of this reinvestigation.

In our hands, sodium borohydride reduction of cage imine **1** afforded a material, mp 70–71 °C, for which we have assigned structure **2** (Scheme I). The infrared and proton NMR spectral data for this compound agreed with the corresponding spectral data for the product that Sasaki et al. obtained via $NaBH_4$ reduction of **1**; however, they proposed a different structure for that product (i.e., the isomeric hexacyclic cage compound **3**, which possesses a bridging *N*-benzyl group).[2] We synthesized **3**, mp 157–158 °C, independently via reduction of **1** with sodium cyanoborohydride in methanolic acetic acid.[3] It is well-known[3,4] that sodium cyanoborohydride reduces iminium ions much more rapidly than carbonyl groups; hence, we propose the N-bridged structure **3** for this reduction product. The spectral data for this reduction product is consistent with our suggested structural formulation, but the spectral data do *not* match the corresponding spectral information given by the Japanese group[2] for the product of sodium borohydride reduction of **1**.

Independent verification of the structure of **3** was obtained via a hydrogenolysis experiment.[5a] Thus, treatment of an ethanol solution of **3** with hydrogen over palladized charcoal catalyst afforded the corresponding secondary amine **4**, whose IR, proton NMR, and carbon-13 NMR spectra were identical in all respects with the corresponding spectra of authentic **4**.[5b]

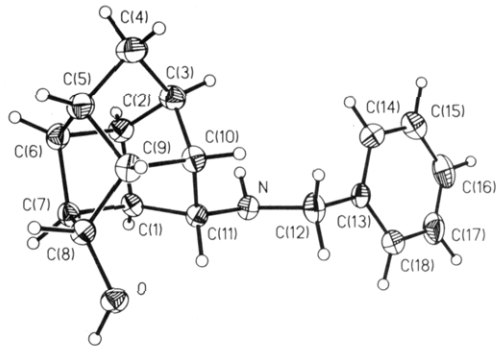


Figure 1. Diagram of **7** as determined by X-ray diffraction.

As was found to be the case for **3**, above, the *N*-benzyl group in **2** also could be hydrogenolyzed via treatment of **2** with hydrogen gas over palladized charcoal. The corresponding oxygen-bridged cage amine, mp 141–143 °C, for which we suggest structure **5**, was thereby obtained. The infrared and proton NMR spectra of the hydrogenolysis product agreed with the corresponding spectra for the material that Sasaki and co-workers obtained from hydrogenolysis of the product of sodium borohydride reduction of **1**; however, they proposed a structure different from **5** for their hydrogenolysis product. We were able to obtain unambiguous confirmation of structure **5** by oxidizing this material to the corresponding nitro ether, **6**, with *m*-chloroperbenzoic acid[6] (MCPBA, Scheme I).

Finally, we investigated the reduction of imine **1** with lithium aluminum hydride. Sasaki and co-workers[2] have assigned structure **2** to the product obtained from this reaction. The material that we obtained, mp 129.5–130 °C, is clearly different from the sample of **2**, mp 70–71 °C,

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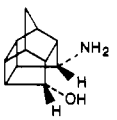
that we synthesized earlier via sodium borohydride reduction of **1**. Partly on the basis of analysis of its proton NMR spectrum, we assign structure **7** to the product of lithium aluminum hydride reduction of **1** (vide infra).

The proton NMR spectrum of **7** displays a triplet at δ 3.91 and a singlet at δ 3.99. Proton NMR spectra obtained in our laboratory for other 8-substituted and 8,11-disubstituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes generally display triplet splitting for *exo*-8,11 protons and little or no fine structure for *endo*-8,11 protons.[7] Accordingly, we assign the triplet at δ 3.91 to the *exo*-8 proton and the singlet at δ 3.99 to the *endo*-11 proton in **7**. This assignment has been confirmed via single-crystal X-ray structural analysis of **7**; a drawing of the structure of **7** thereby obtained appears in Figure 1. Although such exo,endo reduction of the unsaturated groups in **7** may appear to be unusual, it should be noted that similar exo,endo reductions of carbonyl groups have been reported to result via sodium borohydride reduction of a variety of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones.[8]

Compound **7** crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions a = 18.901 (3) Å, b = 6.896 (1) Å, c = 21.338 (2) Å, β = 100.37 (1)°, and Z = 8. The volume of the cell is 2735.9 (5) Å^3, the molecular formula weight is 267.37, and the calculated crystal density is 1.30 g cm^{-3}.

In order to obtain an estimate of the additional strain which the 8,11-substituents in **7** introduce into the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane system, we have performed molecular mechanics calculations[9] on *endo*-8-hydroxy-*exo*-11-aminopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (i.e., the corresponding amine, **9**, derived via debenzylation of **7**) and on the parent hydrocarbon, **8**. The results of these calculations are shown in Table I. Inspection of the data in Table I reveals that the total strain energy in **9** exceeds that of **8** by ca. 5 kcal/mol. Bending and torsional distortions contribute in roughly equal proportion to the total strain energy in **9**.

Table I. Calculated[9] Standard Heats of Formation and Strain Energies in 8 and 9[a]

compound	$\Delta H_f°$ (gas, 298 K), kcal/mol	strain energy, kcal/mol
 **8**	20.67 (21.93,[b] 19.62[c])[d]	53.96[a,e]
 **9**	−12.03	59.02[f]

[a] Previously published calculated values of $\Delta H_f°$ and strain energy for **8** are given in parentheses. [b] Calculated by the method of Schleyer et al.[12] [c] Calculated by the method of Allinger et al.[13] [d] Reference 11. [e] Calculated[9] contributions to strain in **8**: bending, 28.52 kcal/mol; torsion, 30.24 kcal/mol. [f] Calculated[9] contributions to strain in **9**: bending, 30.64 kcal/mol; torsion, 31.96 kcal/mol.

Experimental Section

Melting points are uncorrected.

Reduction of 1 with Sodium Borohydride. Compound **1** was prepared by reacting pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (5.00 g, 28.7 mmol) with benzylamine (3.20 g, 30 mmol) according to the procedure described by Sasaki et al.[2] The material thereby prepared was used without further purification; it was immediately dissolved in a solution of dry methanol (30 mL) in dry tetrahydrofuran (THF, 150 mL). To the resulting solution was added sodium borohydride (1.5 g, 39 mmol) portionwise with stirring at room temperature during 5 min. The resulting mixture was stirred overnight at room temperature. The reaction mixture was concentrated in vacuo, and the residue was partitioned between water (100 mL) and methylene chloride (100 mL). The layers were separated, and the aqueous layer was extracted with methylene chloride (3 × 50 mL). The combined organic layers were washed with water (2 × 100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. A pale yellow oil was thereby obtained. This oil was purified via column chromatography (silica gel stationary phase, 1:1 methylene chloride–hexane mixed solvent as eluent). A pale yellow oil was thereby obtained, which solidified on standing at room temperature to afford a waxy solid (3.76 g, 49%). Recrystallization of this material from benzene–hexane mixed solvent afforded pure **2** as colorless, feathery needles: mp 70–71 °C; IR (KBr) 3320 (sh, m), 1604 (w), 1501 (w), 1476 (m), 1458 (m), 1367 (s), 1354 (s), 1018 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.59 (*AB*, J_{AB} = 13.5 Hz, 1 H), 1.94 (*AB*, J_{AB} = 13.5 Hz, 1 H), 2.22 (br s, 1 H), 2.45 (t, J = 5.2 Hz, 1 H), 2.5–2.7 (m, 4 H), 2.7–2.95 (m, 3 H), 3.99 (*AB*, J_{AB} = 13.5 Hz, 1 H), 4.02 (*AB*, J_{AB} = 13.5 Hz, 1 H), 4.68 (t, J = 5.4 Hz, 1 H), 7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 41.6 (d), 42.1 (d), 43.2 (d), 43.3 (d), 43.3 (t), 44.6 (d), 44.9 (d), 48.9 (t), 54.8 (d), 55.3 (d), 82.5 (d), 109.7 (s), 126.9 (d), 127.9 (d), 128.4 (d), 140.9 (s).

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.74. Found: C, 81.49; H, 7.33.

Hydrogenolysis of 2. Compound **2** (1.00 g, 3.77 mmol) was reacted with hydrogen over 5% palladized charcoal catalyst (0.3 g) in ethanol (30 mL) for 12 h at atmospheric pressure and at room temperature.[2] Workup of the reaction mixture followed by recrystallization of the product from methylene chloride–hexane mixed solvent afforded pure **5** (449 mg, 68%) as colorless platelets: mp 141–143 °C (lit.[2] mp 138–140 °C). The infrared and proton NMR spectra of this material agreed with those reported by Sasaki and co-workers[2] for the product obtained via sodium borohydride reduction of **1** followed by hydrogenolysis. The product obtained via hydrogenolysis of **2** was further characterized via oxidation to the corresponding nitro ether (vide infra).

Hydrogenolysis of 3. A solution of **3** (500 mg, 1.88 mmol) in absolute ethanol (75 mL) was reacted with hydrogen over 10% palladized charcoal (catalytic amount) at 50 psig in a Parr shaker apparatus for 20 h. The reaction mixture was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The residue thereby obtained was recrystallized from acetone to afford pure **4** (0.26 g, 79%). The IR, proton NMR, and carbon-13 NMR spectra of this material were identical with the corresponding spectra that have been reported previously for **4**.[5b]

Oxidation of 5. To a stirred, refluxing solution of MCPBA (0.116 g, 0.63 mmol) in chloroform (20 mL) under nitrogen was added dropwise a solution of **5** (17 mg, 0.096 mmol) in chloroform (5 mL). The resulting mixture was refluxed for 2 h after the addition of substrate had been completed. The reaction mixture was cooled to room temperatue and then washed sequentially with saturated aqueous sodium bisulfate solution (2 × 50 mL), aqueous saturated sodium bicarbonate solution (2 × 50 mL), and water (50 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography (silica gel stationary phase, 1:9 ethyl acetate–hexane mixed solvent as eluent), thereby affording pure **6** (9 mg, 45%) as a colorless microcrystalline solid: mp 120.0–120.5 °C; IR (KBr) 1549 (vs), 1382 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.64 (*AB*, J_{AB} = 10.8 Hz, 1 h), 2.01 (*AB*, J_{AB} = 10.8 Hz, 1 H), 2.8–3.3 (m, 8 H), 4.97 (t, J = 3.6

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Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 41.3 (d), 42.8 (d), 43.3 (t), 44.6 (d), 44.9 (2 C, d), 49.6 (d), 54.7 (d), 59.1 (d), 84.7 (d), 121.2 (s); mass spectrum, m/e (relative intensity) (no molecular ion), 159 (100).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.30; H, 5.47.

Reduction of 1 with Sodium Cyanoborohydride. Compound 1 was prepared by reacting pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (5.00 g, 28.7 mmol) with benzylamine (3.20 g, 30 mmol) according to the procedure described by Sasaki et al.[2] The material thereby prepared was used without further purification; it was immediately dissolved in a solution of acetic acid (15 mL) in dry methanol (250 mL). To the resulting solution was added sodium cyanoborohydride (2.0 g, 32 mmol) portionwise with stirring at room temperature during 5 min. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then concentrated in vacuo, and water (100 mL) was added to the residue. The resulting suspension was stirred, and solid sodium bicarbonate was added portionwise until evolution of carbon dioxide ceased. Excess solid sodium bicarbonate (2.0 g) was added, and the aqueous suspension was extracted with methylene chloride (4 × 50 mL). The combined extracts were washed with water (2 × 100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. A yellow microcrystalline solid was thereby obtained. This material was recrystallized from benzene to afford pure **3** (5.30 g, 70%) as a colorless microcrystalline solid: mp 157-158 °C; IR (KBr) 3115 (br, vs), 3043 (w), 3019 (w), 2948 (s), 2864 (s), 2832 (s), 1603 (m), 1498 (m), 1326 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 1.43 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.76 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.2-2.6 (m, 8 H), 3.29 (t, J = 5.0 Hz, 1 H), 3.37 (*AB*, J_{AB} = 10.5 Hz, 1 H), 3.91 (*AB*, J_{AB} = 10.5 Hz, 1 H), 4.93 (br s, 1 H), 7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 41.7 (t), 41.8 (d), 42.6 (d), 43.2 (d), 44.9 (d), 45.5 (d), 50.8 (d), 51.7 (t), 53.4 (d), 55.1 (d), 64.9 (d), 110.8 (s), 126.7 (d), 128.4 (d), 128.5 (d), 139.2 (s).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.74. Found: C, 81.55; H, 7.50.

Reduction of 1 with Lithium Aluminum Hydride. Compound 1 was prepared by reacting pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (5.00 g, 28.7 mmol) with benzylamine (3.20 g, 30 mmol) according to the procedure described by Sasaki et al.[2] The material thereby prepared was used without further purification; it was immediately dissolved in dry THF (100 mL). To the resulting solution was added lithium aluminum hydride (2.3 g, 60 mmol) portionwise with stirring at room temperature during 10 min. After the addition of the reducing agent had been completed, the reaction mixture was refluxed for 2 h. The reaction mixture was then cooled to room temperature and quenched by cautious, dropwise addition of water (50 mL). Diethyl ether (200 mL) was added, and the resulting mixture was stirred for 15 min. The mixture was filtered, and the residue was washed with ether (25 mL). The combined filtrates were diluted with water (50 mL), and the layers were separated. The aqueous layer was extracted with ether (2 × 50 mL). The combined ethereal solutions were washed with water (50 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo to afford a pale yellow oil. This oil was purified via column chromatography (silica gel stationary phase, diethyl ether as eluent). The first fraction afforded an intractable oil (1.3 g). Continued elution of the chromatography column afforded a second fraction, which contained **2** (780 mg, 10%). Further elution of the chromatography column with 1:10 methanol-methylene chloride mixed solvent afforded a third fraction, from which a yellow microcrystalline solid could be obtained (2.2 g, 29%). This material was recrystallized from methanol-hexane mixed solvent, thereby affording pure **7** as a colorless microcrystalline solid: mp 129.5-130 °C; IR (KBr) 3600-2700 (br, vs), 1604 (w), 1478 (m), 1362 (m), 1112 (m), 1078 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.37 (*AB*, J_{AB} = 11.3 Hz, 1 H), 1.68 (*AB*, J_{AB} = 11.3 Hz, 1 H), 2.2-2.35 (m, 2 H), 2.4-2.5 (m, 2 H), 2.6-2.7 (m, 4 H), 3.47 (s, 1 H), 3.73 (s, 2 H), 3.91 (t, J = 4.0 Hz, 1 H), 3.99 (s, 1 H), 5.32 (s, 1 H), 7.2-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 34.7 (t), 38.6 (d), 39.5 (d), 40.1 (d), 40.5 (d), 43.2 (d), 44.2 (d), 46.4 (d), 46.6 (d), 51.2 (t), 58.3 (d), 73.8 (d), 126.6 (d), 128.0 (d), 128.2 (d), 140.8 (s).

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.67; H, 8.02.

Single-Crystal X-ray Structural Analysis of 7. A crystal of dimensions 0.10 × 0.33 × 0.50 mm was mounted on a Nicolet R3m/μ update of a P2$_1$ diffractometer. Data were collected in the Wyckoff mode (4° ≤ 2θ ≤ 45°, 2θ fixed ω varied) with a scan rate of 4-29.3 deg min^{-1} using Mo Kα radiation (λ = 0.71073 Å). Lattice parameters were obtained from a least-squares refinement of 25 centered reflections (31.29° ≤ 2θ ≤ 40.52°). Systematic absences and Laue symmetry 2/m were consistent with space group $C2/c$. A total of 1792 independent reflections were collected, of which 1254 were ≥3.0$\sigma(I)$. Lorentz-polarization and ψ-scan empirical absorption corrections were applied. The structure was solved by direct-methods techniques and refined by anisotropic block-cascade least-squares techniques (H atoms refined isotropically) to a final R of 0.0489, wR = 0.0483 (256 parameters), S = 1.126, and $(\Delta/\sigma)_{max}$ = 0.019. The largest peaks in the final difference map were +0.21 and -0.17 e Å^{-3}. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $w = [\sigma^2(F_o) + 0.000\,63F_o^2]^{-1}$. The mass absorption coefficient, μ, was determined to be 0.79 cm^{-1} (Mo Kα). All computer programs were supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[10]

Acknowledgment. We gratefully acknowledge the assistance of Dr. Sanjay Basak with the synthesis and characterization of **6**. We thank the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963 to A.P.M., Grant P-074 to W.H.W.), and the University of North Texas Faculty Research Committee for financial support of this study.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, torsion angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters (9 pages); observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Structural Assignment of a Methylcyclopentadiene-Toluquinone Diels-Alder Cycloadduct. Analysis of the Two-Dimensional NMR Spectrum of 1,6-Dimethyl-1α,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-diol

Gary S. Linz, Andrew S. Zektzer, and Gary E. Martin*

Department of Medicinal Chemistry, College of Pharmacy, University of Houston, Houston, Texas 77004

Alan P. Marchand* and Pei-wen Jin

Department of Chemistry, University of North Texas, Box 5068, Denton, Texas 76203

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The tricyclic compounds that result via Diels-Alder cycloaddition of substituted cyclopentadienes to substituted *p*-benzoquinones are of considerable interest as intermediates in the synthesis of natural products.[1-3] As

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