

Assignment of the ^1H and ^{13}C NMR spectra of 1-methyl-6-phenyl-1 α ,4 α ,4 α ,5 α ,8 β ,8 α -hexahydro-1,4-methanonaphthalene-5,8-diol

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Dedicated to Professor Henry J. Shine on the occasion of his 80th birthday

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Abstract

The synthesis of the title compound, **5**, a tricyclic diol, is described. The ^1H and ^{13}C NMR spectra of **5** have been analyzed, and individual spectral resonance signals have been assigned to specific ^1H and ^{13}C nuclei, respectively, in this compound.

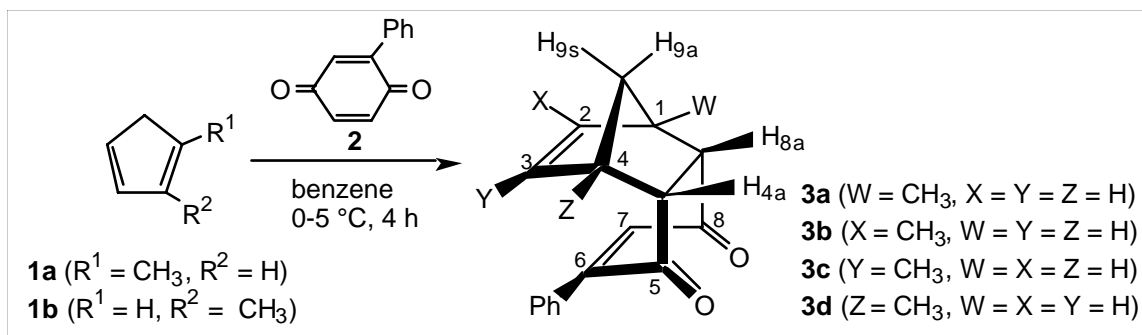
Keywords: ^1H and ^{13}C NMR spectral assignments, tricyclic diol

Introduction

1,4-Methanonaphthalene derivatives (i.e., functionalized *endo*-tricyclo[6.2.1.0^{2,7}]undecanes) are of intense current interest as intermediates in the synthesis of natural products.¹⁻³ Pursuant to our continuing interests in the synthesis and chemistry of novel polycarbocyclic "cage" compounds,⁴ several substituted 1,4-methanonaphthalenes have been prepared.⁵ In addition, we have reported the results of detailed NMR studies of several compounds of this general type.^{1b,6}

In the present study, Diels-Alder reaction of a mixture of 1- and 2-methylcyclopentadienes (i.e., **1a** and **1b**, respectively)⁷ with 2-phenyl-2-benzoquinone (**2**) has been investigated. Preferential cycloaddition of **1a** and **1b** to the less highly substituted C=C double bond in **2**² potentially could lead to the formation of as many as four isomeric *endo* [4 + 2] cycloadducts (i.e., **3a-3d**, Scheme 1).^{5c} Column chromatographic separation of the mixture of cycloadducts obtained from this reaction afforded a single, isomerically pure cycloadduct, **3a** (*vide infra*), mp 77-78 °C.

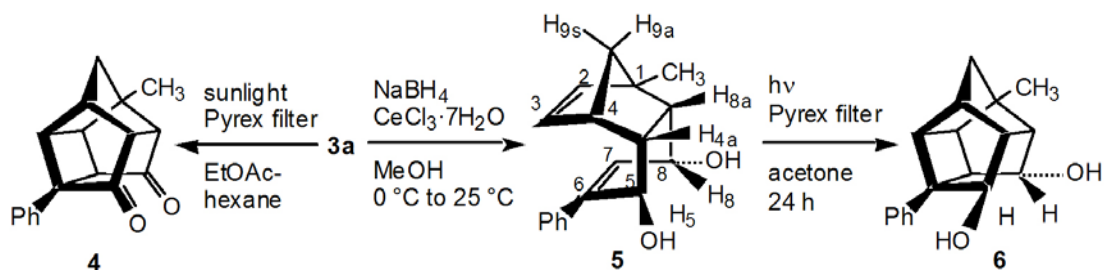
The fact that this cycloadduct indeed possesses the *endo* configuration was demonstrated by its facile intramolecular [2 + 2] photocyclization to the corresponding pentacyclic cage diol. Thus, 3-methyl-7-phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**4**, mp 116-117°C) was formed by irradiating **3a** with Pyrex-filtered sunlight. The structure of **4** has previously been established unequivocally via application of single crystal X-ray structural techniques.^{5d} Thus, we conclude that the material isolated from the mixture of products derived via Diels-Alder cycloaddition of a mixture of **1a** and **1b** to **2** indeed possesses structure **3a** (Scheme 1).



Scheme 1

The reaction of **3a** with $\text{NaBH}_4\text{-CeCl}_3$ ⁸ resulted in highly stereoselective reduction of both ketone C=O groups, thereby affording a single tricyclic diol, i.e., **5**, mp 100.5-101.5 °C. Subsequent irradiation of this diol resulted in facile intramolecular [2 + 2] photocyclization, thereby affording the corresponding cage diol, **6**, mp 166-167 °C (Scheme 2). The structure of **6** previously has been established unequivocally via single crystal X-ray structural analysis.^{5d}

Armed with this pertinent structural information, a detailed NMR study of tricyclic diol **5** was undertaken in an effort to assign all individual resonance signals in its ¹H and ¹³C NMR spectra. The results of this study are described below.



Scheme 2

Results and Discussion

NMR spectral assignments were made by using ^1H - ^1H spin-spin coupling constant data together with information derived (i) by application of nuclear magnetic double resonance (NMDR) experiments, (ii) from a DEPT experiment,⁹ and (iii) from 2D COSY and long-range HETCOR¹⁰ spectra of **5**. There are three well-resolved vinyl proton resonances in the ^1H NMR spectrum of **5** (δ 5.97, 6.15, and 6.50; see Figure 1). Inspection of the COSY spectrum (Figure 2) reveals that the resonance at δ 5.97 correlates strongly with that at δ 6.15 [i.e., H(2), H(3)], thereby permitting the remaining resonance signal at δ 6.50 to be assigned to H(7). Inspection of the HETCOR spectrum of **5** reveals that H(7) correlates with the ^{13}C resonance at δ 131.3, which thus can be assigned to C(7).

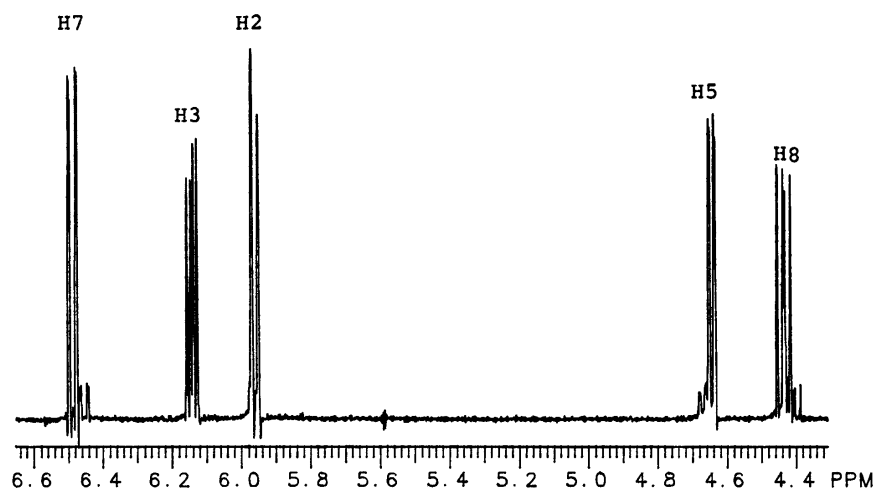


Figure 1. Expanded downfield region of the 300 MHz ^1H NMR spectrum (resolution enhanced) of **5**.

The norbornene C=C vinyl protons, H(2) and H(3), are readily distinguished by inspection of their spin-spin coupling patterns. Thus, the absorption signal at δ 6.15 [H(3)] displays two vicinal couplings [$^3J_{\text{H}(2)\text{H}(3)} = 5.5$ Hz, $^3J_{\text{H}(3)\text{H}(4)} = 3.1$ Hz], whereas the signal at δ 5.97 [H(2)] displays one vicinal [$^3J_{\text{H}(2)\text{H}(3)} = 5.5$ Hz] and one allylic [$^4J_{\text{H}(2)\text{H}(4)} = 0.9$ Hz] coupling. Double irradiation of the proton signal at δ 2.81 [H(4)] causes the signals that correspond to H(2) and H(3) to collapse into a simple AB pattern [$J_{\text{AB}} = 5.5$ Hz]. Inspection of the corresponding HETCOR spectrum of **5** permits assignment of the ^{13}C signals at δ 138.0, 133.4, and 45.5 to C(2), C(3), and C(4), respectively.

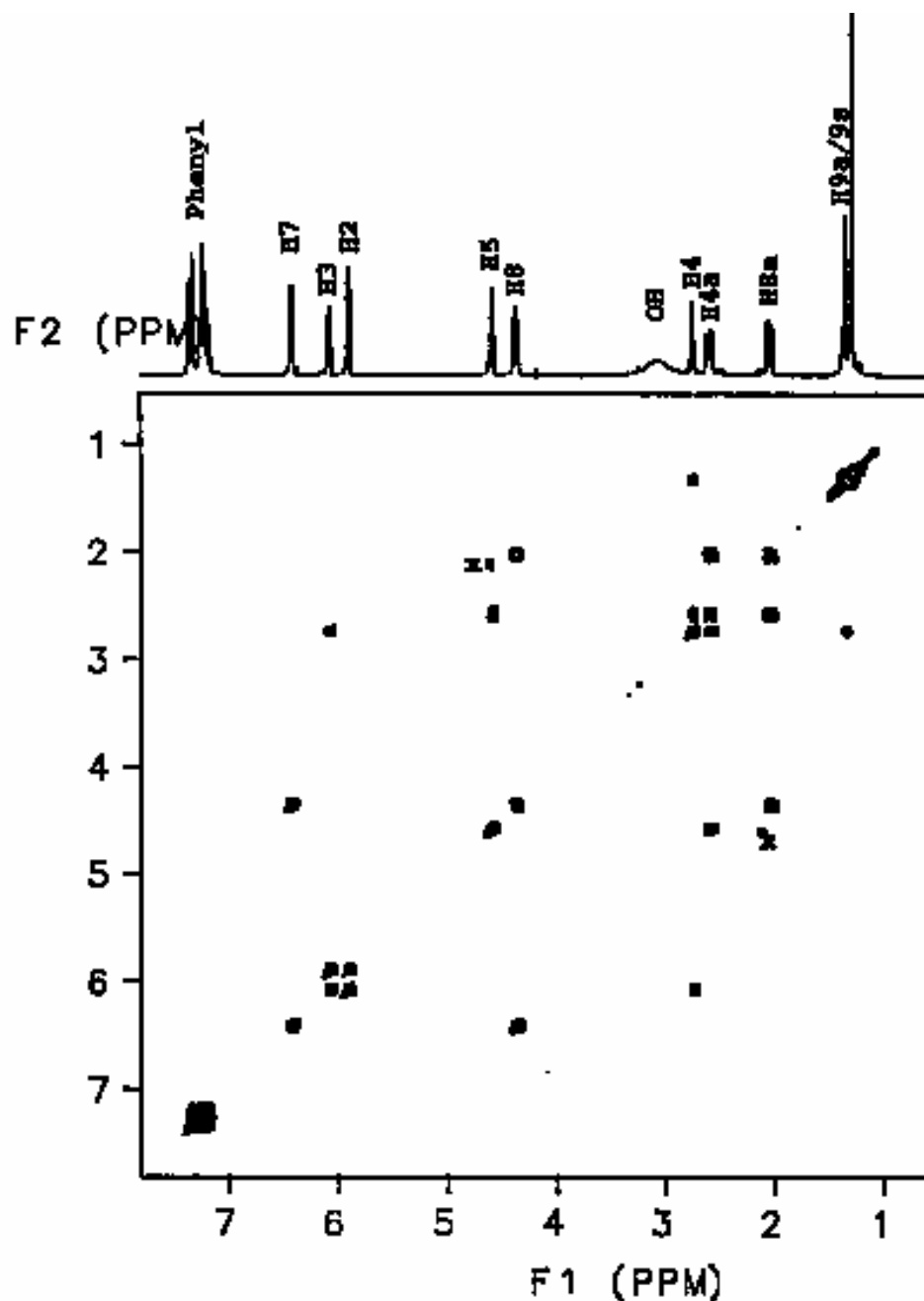


Figure 2. 2D COSY spectrum of **5**.

The results of a DEPT experiment⁹ permit assignment of the peaks at δ 52.3 (s), 59.5 (t), and 17.7 (q) to C(1), C(9), and the C(1)-CH₃ methyl carbon atoms, respectively. The methyl group protons appear as a singlet at δ 1.34, and the bridging methylene protons, H(9a) and H(9s) appear as an unresolved multiplet centered at δ 1.41 in the ¹H NMR spectrum of **5**. Double irradiation of the proton signal at δ 2.81 [H(4)] causes the signal that corresponds to H(9a) and H(9s) to collapse to an AB pattern [δ_A 1.39; δ_B 1.42; J_{AB} = 7.9 Hz]. We are not able to further

assign these two resonance signals, i.e., δ_A and δ_B , to individual protons H(9a) and H(9s) with certainty.

Inspection of the long-range HETCOR spectrum of **5** (optimized for $^3J_{CH}$ couplings) permits assignment of H(4a) and H(8a). The ^{13}C NMR resonance signal at δ 138.0 [C(2)] displays $^3J_{CH}$ correlations with the CH_3 protons and also with the proton signals that appear at δ 1.41 [H(9a), H(9s)], 2.11 [H(4) or H(8a)] and 2.81 [H(8a) or H(4)]. Since the signal at δ 2.81 correlates with the signal at δ 6.15 [H(3)] in the COSY spectrum of **5**, the resonance signal at δ 2.81 can be assigned to H(4). Thus, the remaining 1H NMR signal at δ 2.11 must correspond to H(8a).

In addition, inspection of the long-range HETCOR spectrum reveals the existence of three-bond correlations between the ^{13}C NMR resonance at δ 133.4 [C(3)] and the proton signals at δ 1.41 [H(9a), H(9s)] and 2.66, respectively. Thus, the resonance signal at δ 2.66 can be assigned to H(4a). Inspection of the HETCOR spectrum also permits assignment of the ^{13}C resonance signals at δ 49.1 and 50.3, which correlate with H(4a) and H(8a), respectively.

Assignments of protons H(5) and H(8) follow from inspection of the COSY spectrum of **5**. Here, the signal at δ 2.11 [H(8a)] is seen to correlate with peaks at δ 2.66 [H(4a)] and 4.45 [which we assign to H(8)]. Proton H(8a) appears as a double doublet; the larger of the two couplings ($J_1 = 10.9$ Hz) is to H(4a), whereas the smaller ($J_2 = 4.9$ Hz) is to H(8). The signal at δ 2.66 [H(4a)] correlates with three resonances, i.e., δ 2.11 [H(8a), $J_1 = 10.9$ Hz], 2.81 [H(4), $J_2 = 4.8$ Hz], and 4.65 [$J_3 = 3.3$ Hz, which we assign to H(5)]. Inspection of the HETCOR spectrum permits assignment of the ^{13}C resonance signals at δ 69.0 and 63.3, which correlate with H(5) and H(8), respectively.

Only one vinyl carbon [C(6)] and the aromatic carbon resonances remain to be assigned. Data contained in the long-range HETCOR spectrum permits these assignments to be made with confidence. Thus, two long-range 1H - ^{13}C correlations appear, both of which involve the ^{13}C resonance signal at δ 148.9. One of these is a $^3J_{CH}$ coupling to the proton resonance signal at δ 4.45 [H(8)], and the other is a $^2J_{CH}$ correlation with the proton signal at δ 4.65 [H(5)]. Hence, the ^{13}C resonance signal at δ 148.9 is assigned to C(6).

The lone remaining downfield singlet in the proton noise-decoupled ^{13}C NMR spectrum of **5** (at δ 140.0) therefore corresponds to the *ipso* aromatic carbon atom. Other aromatic carbon resonance signals appear as doublets at δ 125.6, 127.6, and 128.4.

Finally, the broad singlet at δ 2.97 in the 1H NMR spectrum of **5** is assigned to the proton signals associated with the OH groups. This assignment is supported by the fact that this peak disappears from the spectrum upon addition of a few drops of D_2O to the NMR sample tube that contains a $CDCl_3$ solution of **5**.

Approximate values of the torsion angles along bonding pathways H(4a)-C(4a)-C(5)-H(5) and H(8a)-C(8a)-C(8)-H(8) can be estimated from published X-ray data for 1,6-dimethyl-1 α ,4 α ,5 α ,8 β ,8 α -hexahydro-1,4-methanonaphthalene-5,8-diol,^{5a} a compound whose overall molecular structure is closely analogous to that of **5**. The values of these two torsion angles as estimated in this fashion are 40.8° and -43.4°, respectively.¹¹ By using molecular mechanics calculations based upon Allinger's MM2 force-field¹² in PCMODEL,¹³ we can estimate the

analogous torsion angles in **5** to be 43° and -40° , respectively. These angles correspond to calculated couplings constants of ${}^3J_{\text{H}(4a)\text{H}(5)} = 3.89$ Hz and ${}^3J_{\text{H}(8a)\text{H}(8)} = 4.32$ Hz (obtained by using Altona¹⁴ equations, which are contained within the PCMODEL program). Thus, the observed magnitudes of the two vicinal couplings ${}^3J_{\text{H}(4a)\text{H}(5)}$ and ${}^3J_{\text{H}(8a)\text{H}(8)}$ (i.e., 4.8 and 4.9 Hz, respectively) suggest that each pair of mutually coupled protons is oriented *cis* (rather than *trans*).

The same computational approach was applied to the isomer of **5** in which the configurations of both C(5) and C(8) were inverted. For this *cis* diol (with *exo*-OH groups), the torsion angles along bonding pathways H(4a)-C(4a)-C(5)-H(5) and H(8a)-C(8a)-C(8)-H(8) were calculated (PCMODEL) to be 171° and -166° , respectively, with associated coupling constants of 10.23 and 9.75 Hz, respectively. Clearly, these calculations support the NMR coupling constant data upon which the suggested stereochemistries of the C(5)-OH and C(8)-OH bonds in **5** are based and also the conclusions derived from X-ray data for **6**.^{5d}

Summary and Conclusions

Proton and ${}^{13}\text{C}$ NMR spectra of **5** have been assigned by using ${}^1\text{H}$ - ${}^1\text{H}$ and ${}^1\text{H}$ - ${}^{13}\text{C}$ coupling constant data together with information derived (i) by application of nuclear magnetic double resonance (NMDR) experiments, (ii) from data obtained by using a DEPT⁹ experiment, and (iii) from relevant 2D COSY and long-range HETCOR¹⁰ spectra. These spectral assignments are summarized in Table 1. Conclusions regarding the stereochemistry of the C(5)-OH and C(8)-OH bonds in **5** are supported by the results of molecular mechanics calculations.

Table 1. Proton and carbon chemical shifts and coupling constants in **5**

Proton Position	Chemical shift (δ)	Peak Multiplicity	Carbon Position	Chemical shift (δ)	Peak Multiplicity
2	5.97	doubled AB ($J_{AB} = 5.5$ Hz, $J_1 = 0.9$ Hz)	1	52.3	singlet
3	6.15	doubled AB ($J_{AB} = 5.5$ Hz, $J_1 = 3.1$ Hz)	2	138.0	doublet
4	2.81	complex multiplet	3	133.4	doublet
4a	2.66	doubled doublet ($J_1 = 10.9$ Hz, $J_2 = 4.8$ Hz, $J_3 = 3.3$ Hz)	4	45.5	doublet
5	4.65	doubled doublet ($J_1 = 4.8$ Hz, $J_2 = 1.1$ Hz)	4a	49.1	doublet
7	6.50	doubled doublet ($J_1 = 6.6$ Hz, $J_2 = 1.1$ Hz)	5	69.0	doublet
8	4.45	doubled doublet ($J_1 = 6.6$ Hz, $J_2 = 4.9$ Hz)	6	148.9	singlet
8a	2.11	doubled doublet ($J_1 = 10.9$ Hz, $J_2 = 4.9$ Hz)	7	131.3	doublet
9a,9s	1.41	complex multiplet	8	63.3	doublet
CH ₃	1.34	singlet	8a	50.3	doublet
Ph	7.25-7.50	complex multiplet (5 H)	9	59.5	triplet
OH	2.97	broad singlet	CH ₃	17.7	quartet
			Ph	140.0	singlet
				(<i>ipso</i>)	
			Ph	128.4	doublet
			Ph	127.6	doublet
			Ph	125.6	doublet

Experimental Section

General Procedures. Melting points are uncorrected. Elemental microanalyses were performed by personnel at Galbraith Laboratories, Inc., Knoxville, TN.

1-Methyl-6-phenyl-1 α ,4 α ,4 α ,8 α -tetrahydro-1,4-methanonaphthalene-5,8-dione (3a). A solution of 2-phenyl-*p*-benzoquinone (**2**, 5.0 g, 27 mmol) in benzene (60 mL) was cooled to 0-5 °C via application of an external ice-water bath. To this cooled solution was added with stirring freshly cracked methylcyclopentadiene dimer⁷ (2.18 g, 27 mmol). The resulting mixture was stirred at 0-5 °C during 4 h and then was concentrated *in vacuo*. The crude product, a mixture of

[4 + 2] cycloadducts, was obtained as a yellow oil (6.47 g, 90%). This material was purified via flash column chromatography on silica gel by eluting with 5% EtOAc-hexane. Pure **3a** (2.88 g, 40%) was thereby obtained as a yellow microcrystalline solid: mp 77-78 °C; IR (KBr) 3005 (m), 1655 (vs), 1618 (m), 1460 (m), 1360 (w), 1275 (s), 1105 (m), 780 (m), 760 (m), 735 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 1.55 (AB, *J*_{AB} = 8.6 Hz, 1 H), 1.49 (AB, *J*_{AB} = 8.6 Hz, 1 H), 1.60 (s, 3 H), 2.98 (d, *J* = 8.6 Hz, 1 H), 3.45-3.57 (m, 2 H), 5.91 (d, *J* = 6.5 Hz, 1 H), 6.04-6.13 (m, 1 H), 7.15 (s, 1 H), 7.32-7.50 (m, 5 H); ¹³C NMR (CDCl₃) δ 17.3 (q), 49.97 (d), 52.04 (d), 53.8 (d), 55.7 (t), 58.1 (s), 128.5 (d), 128.9 (d), 130.1 (d), 133.5 (s), 134.8 (d), 139.1 (d), 139.8 (d), 151.5 (s), 199.3 (s), 199.7 (s). Mass spectrum *m/z* (relative intensity) (no parent ion) 184 (75), 156 (55), 128 (47), 102 (49), 82 (100), 76 (26), 54 (91). Anal. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.40; H, 6.13.

Intramolecular [2 + 2] photocyclization of **3a** afforded **4**, whose structure has previously been established unequivocally via application of single crystal X-ray structural techniques.^{5d}

1-Methyl-6-phenyl-1 α ,4 α ,4 α ,5 α ,8 β ,8 α -hexahydro-1,4-methanonaphthalene-5,8-diol (5). A solution of **3a** (1.85 g, 7.00 mmol) and CeCl₃·7H₂O (50 mL of a 0.60 M solution in MeOH, 30 mmol) was placed in a 250 mL round-bottom flask, which then was cooled to 0-5 °C via application of an external ice-water bath. To this cooled solution was added portionwise with stirring powdered NaBH₄ (570 mg, 28 mmol) in such a manner that the temperature of the reaction mixture did not exceed 5 °C. After the addition of NaBH₄ had been completed, the external ice-water bath was removed, and the stirred reaction mixture was allowed to warm gradually to ambient temperature during 0.5 h. Thin layer chromatographic (tlc) analysis of the reaction mixture indicated the absence of starting material (**3a**). The reaction was quenched via careful, portionwise addition of distilled water (50 mL). The resulting aqueous suspension was extracted with CH₂Cl₂ (5 × 40 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. Crude **5** thereby obtained was further purified via flash column chromatography on silica gel by eluting with 1:12 EtOAc-hexane. Fractional recrystallization of the eluate from EtOAc-hexane afforded pure **5** (1.5 g, 80%) as a colorless microcrystalline solid: mp 100.5-101.5 °C; IR (KBr) 3235 (s), 2930 (s), 1455 (m), 1360 (m), 1300 (m), 1170 (m), 1140 (m), 1030 (s), 950 (m), 780 (s), 720 cm⁻¹ (s); ¹H NMR (CDCl₃) and ¹³C NMR (CDCl₃): See Table 1. Anal. Calcd for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.28; H, 7.51.

Intramolecular [2 + 2] photocyclization of **5** afforded **6**, whose structure has previously been established unequivocally via application of single crystal X-ray structural techniques.^{5d}

Acquisition of NMR spectral data. Proton and ¹³C NMR spectra were recorded on Varian XL-300 and Varian VXR-300 NMR spectrometers by using 10% solutions in CDCl₃ with Me₄Si internal standard. All 1D and 2D NMR pulse sequences were run by using standard software supplied by Varian Associates, Inc., version 6.1d. COSY spectra were obtained with spectral windows of 2186.3 Hz in both dimensions, acquisition times of 0.23 s, 256 increments with 16 transients per increment, a delay of 2.0 s between transients, and data processed as 1024 × 1024 matrices. HETCOR and long-range HETCOR spectra were obtained by using acquisition times

of 0.1 s, 256 increments with 64 transients per increment, a delay of 3.0 s between transients, and data processed as 2048 x 512 matrices. Long-range HETCOR experiments, performed by using a value of 8 Hz for the average long-range J_{CH} , resulted in the acquisition of cross-peaks that correspond almost exclusively to three-bond correlations, $^3J_{CH}$.

Acknowledgments

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