Pergamon

Tetrahedron 54 (1998) 12691–12698

TETRAHEDRON

Thiele's Acid Revisited: Isolation and Characterization of Two Minor Products Formed by Carbonation of Cyclopentadienide Anion

Alan P. Marchand, * I. N. N. Namboothiri, and Scott B. Lewis

Department of Chemistry, University of North Texas, Denton, Texas 76203-0068

William H. Watson* and Mariusz Krawiec

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129-8860

Received 9 June 1998; revised 27 July 1998; accepted 3 August 1998

Abstract. Carbonation of sodium cyclopentadienide leads to the formation of 3aα,4α,7α,7aα-tetrahydro-4,7-methano-1*H*-indene-2,6-dicarboxylic acid [i.e., "Thiele's acid", **2i** (R = H), 60%] along with several isomeric $C_{12}H_{12}O_4$ minor products. The dimethyl esters of two of these minor products, i.e., dimethyl 3aα,4α,7α,7aα-tetrahydro-4,7-methano-1*H*-indene-2,4-dicarboxylate [**2a** (R = Me), 13%) and the corresponding 3a,6-dicarboxylate [**2n** (R = Me), 1%] have been isolated and characterized. Intramolecular [2 + 2] photocyclization of **2a** (R = Me) afforded **3a** (R = Me) (30%), whose structure was established unequivocally by application of X-ray crystallographic techniques.

Introduction. Almost a century ago, Thiele[1] reported that carbonation of cyclopentadienylpotassium affords a Diels-Alder dimer of cyclopentadienecarboxylic acid, $C_{12}H_{12}O_4$. The structure of this compound subsequently was established as 3aα,4α,7α,7aα-tetrahydro-4,7-methano-1*H*-indene-2,6-dicarboxylic acid ["Thiele's acid"; see **2i** (R = H) in Table 1] by application of chemical[2] and NMR spectroscopic[3] methods. Thiele's acid has been employed as a key intermediate in the synthesis of several novel polycarbocyclic compounds.[4]

In 1959, Peters[5] prepared the corresponding methyl ester of **2i** (R = H) [i.e., "Thiele's ester", **2i** (R = Me)[1b]] by (i) carbonation of cyclopentadienylmagnesium bromide followed by (ii) esterification of the resulting product by using MeOH-H_2SO_4. The diester thereby obtained was purified by vacuum distillation. The distillate, which solidified upon standing, was further purified by fractional crystallization and subsequent column chromatographic purification of the mother liquor. In addition to the major product, Peters[5] also isolated a minor product, mp 103-104 °C, which proved to be isomeric with Thiele's ester.

Based solely upon his analysis of the UV spectrum of the minor reaction product, Peters[5] concluded that only one of the two CO_2Me groups present in this product, i.e., that which is situated in the cyclopentene ring, is conjugated with the (adjacent) carbon-carbon double bond. The remaining CO_2Me group resides in the norbornene moiety and is not conjugated with the norbornene C=C double bond.

Peters[5] suggested structure **2a** (R = Me) (see Table 1) for this minor reaction product. It should be noted that his suggestion is not supported by other experimental or spectroscopic evidence in addition to its UV spectrum. Furthermore, there is more than one possible Diels-Alder dimer of cyclopentadienecarboxylic ester that

0040-4020/98/$ - see front matter
PII: S0040-4020(98)00770-4

fulfills the conditions of Peters' conclusion, i.e., that the minor reaction product contains two CO_2Me groups, only one of which is conjugated with an adjacent C=C double bond (*vide infra*). As part of a program that employs Thiele's ester as a reagent in organic synthesis[4] we have reinvestigated the "minor reaction product" [formulated as **2a** (R = Me) by Peters[5]] in an effort to establish its structure unequivocally.

Results and Discussion. In the present study, a mixture of Diels-Alder dimers of cyclopentadienecarboxylic acid dimers [i.e., compounds of the type **2** (R = H)] was prepared by carbonation of sodium cyclopentadienide. A dilute acetone solution of the mixture of diacids thereby obtained subsequently was irradiated with a Hanovia 450 medium pressure Hg lamp, thereby affording a mixture of intramolecular [2 + 2] photocycloadducts [i.e., pentacyclo-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanedicarboxylic acids of the type **3** (R = H)]. The crude photocyclization product was dissolved in aqueous $NaHCO_3$, and the resulting solution was rendered acidic by dropwise addition of 6 *N* aqueous H_2SO_4 until turbidity appeared. The resulting suspension was allowed to stand overnight to com-plete precipitation of the solid reaction product(s). This precipitate then was isolated by suction filtration and subsequently was air-dried. The material thereby obtained, the minor reaction product, was isolated in *ca.* 4% yield. The filtrate subsequently was acidified by addition of excess 6 *N* aqueous H_2SO_4, thereby affording **3i**[2], the major reaction product, in 64% yield (see the Experimental Section).

Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were obtained for the minor reaction product. The proton-noise decoupled ^{13}C NMR spectrum of this material contains only six carbon resonances, thereby indicating that this compound possesses a twofold symmetry element.

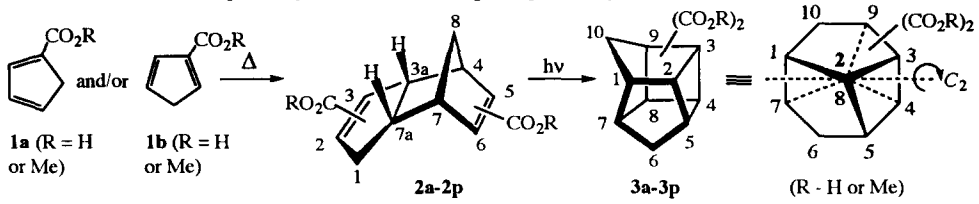
If it is assumed that Diels-Alder dimerization of 1- and 2-cyclopentanecarboxylic acids [i.e., **1a** (R = H) and **1b** (R = H), respectively] proceeds in accordance with the familiar Alder-Stein "principle of maximum accumulation of unsaturation",[6] then it follows that any (or all) of 16 possible *endo* [4 + 2] cycloadducts, **2a-2p** (R = H) could be formed (see Table 1). Subsequent intramolecular [2 + 2] photocyclization of **2a-2p** (R = H) would afford **3a-3p** (R = H), respectively (Table 1). Inspection of the various structures shown in Table 1 reveals that only four of the sixteen possible isomeric pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanedicarboxylic acids, i.e., **3a** (R = H), **3b** (R = H), **3n** (R = H), and **3p** (R = H), possess a twofold symmetry element (C_2 axis).

In order to firmly establish the structure of this photocycloadduct, it was converted into the corresponding bis(*p*-nitrobenzyl ester) derivative. Single crystal X-ray crystallographic analysis of the resulting cage diester established its structure unequivocally to be that of di(*p*-nitrobenzyl) pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-dicarboxylate [i.e., **3a** (R = *p*-nitrobenzyl); see the Experimental Section].

The crude mixture of Diels-Alder cycloadducts [which contains isomeric tricyclic dicarboxylic acids of the type **2a-2p** (R = H)] displayed only limited solubility in acetone, thereby hindering our attempts to scale-up the [2 + 2] photocyclization reaction. For this reason, we found it expedient to convert the mixture of diacids of the type **2** (R = H) into the corresponding methyl esters, since the corresponding diesters display improved solubility in acetone [the solvent of choice for their subsequent intramolecular [2 + 2] photocyclization to compounds of the type **3** (R = H)].

Thus, reaction of isomeric diacids of the type **2** (R = H) with MeOH-H_2SO_4 afforded a corresponding mixture of tricyclic diesters (i.e., compounds of the type **2**, (R = Me). Workup of the reaction mixture afforded Thiele's ester in 60% yield (see the Experimental Section). The remaining mother liquor was further purified by column chromatography. Three chromatography fractions were collected; the first fraction, an oil, consisted of

Table 1. Structures of the 16 possible *endo* [4 + 2] cycloadducts, **2a-2p**, that could be formed by Diels-Alder cycloaddition of the four possible (diene + dienophile) combinations of **1a** and **1b** and their corresponding intramolecular [2 + 2] photocycloadducts (**3a-3p**, respectively)



1a (R = H or Me) **1b** (R = H or Me) **2a-2p** **3a-3p** (R - H or Me)

Diene	Dienophile	*endo* [4 + 2] Cycloadduct	[2 + 2] Cycloadduct	[2 + 2] Cage Point Symmetry
1a	**1a**	**2a** (2,4)	**3a** (5,9)	C_2
		2b (7,7a)	**3b** (1,7)	C_2
		2c (4,7a)	**3c** (7,9)	
		2d (2,7)	**3d** (1,5)	
1a	**1b**	**2e** (3,4)	**3e** (4,9)	
		2f (3a,4)	**3f** (8,9)	
		2g (3,7)	**3g** (1,4)	
		2h (3a,7)	**3h** (1,8)	
1b	**1a**	**2i** (2,6)	**3i** (2,5)	
		2j (6,7a)	**3j** (2,7)	
		2k (2,5)	**3k** (3,5)	
		2l (5,7a)	**3l** (3,7)	
1b	**1b**	**2m** (3,6)	**3m** (2,4)	
		2n (3a,6)	**3n** (2,8)	C_2
		2o (3a,5)	**3o** (3,8)	
		2p (3,5)	**3p** (3,4)	C_2

an inseparable mixture of two isomeric compounds, **A** and **B** (total yield 2%; *vide infra*). Workup of the second fraction afforded a colorless microcrystalline solid, **C** (1.1% yield), mp 99-100 °C. Finally, workup of the third fraction produced an oil, **D**, which was isolated in 13% yield). Analysis of the ^1H and ^{13}C NMR spectra of each of the three chromatography fractions revealed that all of the reaction products **A** - **D** are isomeric with Thiele's ester (*vide infra*).

Determination of the Structures of Isomers C and D. Inspection of the ^1H NMR spectra of pure **C** and pure **D** indicates that each isomer contains one α,β-unsaturated (i.e. "conjugated") ester moiety and also one non-

conjugated ester group. In addition, inspection of the ^{13}C NMR spectrum of the product formed by intramolecular [2 + 2] photocyclization of either **C** or **D** reveals in each case that the resulting cage diester of the type **3** (R = Me) contains a twofold symmetry element.

Once again, it should be noted that among the 16 isomeric cage diesters of the type **3**, only **3a, 3b, 3n** and **3p** (R = Me), possess a twofold symmetry element (C_2 axis). Upon further inspection of the structural information in Table 1, it is evident that only **2a** and **2n** (R = Me) meet the following criteria: (i) both **2a** and **2n** (R = Me) contain one conjugated and one non-conjugated CO_2Me group and (ii) photolysis of either **2a** or **2n** (R = Me) will produce a substituted dimethyl pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-dicarboxylate [i.e., **3a** or **3n** (R = Me), respectively] that possesses a twofold symmetry element.

In order to complete the assignment of the structures of **C** and **D**, the parent cage diacid, **3a** (R = H) from which **3a** (R = *p*-nitrobenzyl) had been synthesized previously (*vide supra*) was esterified by using MeOH-H_2SO_4. The IR, ^1H NMR, and ^{13}C NMR spectra of the cage dimethyl ester thereby obtained [i.e., **3a** (R = Me)] proved to be identical in all respects with the corresponding spectra obtained for the product of intramolecular [2 + 2] photocyclization of **D**. We conclude from this exercise that isomer **D** possesses structure **2a** (R = Me), and since only one other possibility remains, isomer **C** must possess structure **2n** (R = Me).[7]

Some Observations Regarding Compounds A and B. All attempts to separate isomers **A** and **B** by using fractional recrystallization and/or column chromatography proved futile. However, analysis of relevant ^1H NMR and ^{13}C (normal and gated-decoupled) NMR spectra indicate that **A** and **B** were formed as a *ca.* 50-50 mixture of isomers. Furthermore, it is clear from inspection of the NMR spectra that both **A** and **B**, like **2a** and **2n** (i.e., **D** and **C**, respectively), contain one conjugated and one non-conjugated CO_2Me group. Inspection of Table 1 reveals that there are six remaining structures that fit the NMR spectral information for **A** and **B** (i.e., **2d**, **2e**, **2g**, **2j**, **2l** and **2o** (R = Me).

In our hands, photolysis of a mixture of **A** and **B** afforded a mixture of the corresponding cage diesters, **E** and **F**, which also proved to be inseparable by fractional recrystallization and/or column chromatography. Analysis of relevant ^1H NMR and ^{13}C (normal and gated-decoupled) NMR spectra indicate that **E** and **F** were formed in the ratio **E** : **F** = 2.5 : 1. We speculate that the change in ratio of products **E** : **F** *vis-à-vis* that of the starting materials (i.e., **A** : **B** = 1 : 1) may be due to partial decomposition of one of the isomeric starting materials that occurred during photolysis.

It is important to note that intramolecular photocyclization of any of the six possible isomers that might correspond to either **A** or **B** would necessarily result in the formation of the corresponding cage diester [i.e., **3d**, **3e**, **3g**, **3j**, **3l**, or **3o** (R = Me)] which lacks any twofold symmetry element. Indeed, as expected, neither **E** nor **F** contains a twofold symmetry element. The NMR spectral information garnered in this study are insufficient to permit unique identification of the structures of **A**, **B**, **E**, and/or **F**.

Summary and Conclusions. Two minor isomers of Thiele's ester, i.e., **2a** [UV: λ_{max}(EtOH) 222 (log ε 3.69)] and **2n** [UV: λ_{max}(EtOH) 231 (log ε 3.79)], have been isolated and fully characterized. In the course of this study, new cage diester **3a** (R = *p*-nitrobenzyl) was synthesized, and its structure was established unequivocally by application of X-ray crystallographic methods.

Finally, it is instructive to compare our results and conclusions with those forwarded by Peters, who previously reported the isolation and UV spectral characterization of a minor product, mp 103-104 °C, that accompanies the formation of Thiele's ester (see the Introduction).[5] Primarily on the basis of UV spectral

evidence [λ_{max}(EtOH) 230 (log ε 3.81)], Peters suggested that this compound possesses structure **2a** (R = Me). However, in the present study, we find λ_{max}(EtOH) 222 (log ε 3.69) for **2a**.

In the present study, we found that **2a** and **2n** elute on a tlc plate with very similar retention times. The similarity between (i) the yield of "minor isomer" reported by Peters[5] (i.e., *ca.* 20%) and our combined yield of **2a** + **2n** (*ca.* 14%) and (ii) the UV spectral data reported by Peters[5] and that which we report herein for **2n** together suggest to us that the solid compound that Peters[5] isolated and whose melting point and UV spectrum he reported may indeed correspond with **2n** rather than with **2a**. We conjecture that Peters, in fact, may have isolated **2a** in admixture with **2n**. During subsequent work-up and purification, solid **2n** may have crystallized from this mixture, and we conjecture that it is this compound that Peters subsequently characterized.

Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ. High-resolution mass spectral data were obtained at the Mass Spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin by using a ZAB-E double sector high-resolution mass spectrometer (Micromass, Manchester, England) that was operated in the chemical ionization mode by using methane as CI reagent gas. UV spectra were recorded on a Hewlett Packard Diode Array UV-visible spectrophotometer, Model No. 8450A.

Carbonation of Sodium Cyclopentadienide. A solution of freshly cut Na metal (28 g, 1.2 g-atom) in xylene (300 mL) under argon was refluxed briefly with vigorous stirring. The resulting dispersion of Na in xylene under argon was cooled rapidly to ambient temperature. Xylene was decanted by syringe and was replaced with dry THF (300 mL). The resulting mixture was cooled to 0 °C by application of an external ice-water bath. To this cooled mixture was added portionwise with vigorous stirring freshly cracked[8] cyclopentadiene (81.5 mL, 1.25 mol). After all of the diene had been added, the external cold bath was removed, and the reaction mixture was allowed to warm slowly to ambient temperature with stirring overnight. The reaction mixture was poured over excess dry ice and then was allowed to warm gradually to ambient temperature. Water was added, and the phases were separated. Excess 6 *N* aqueous H_2SO_4 (300 mL) was added to the water layer, and the resulting precipitate was collected by suction filtration. This material was air-dried to afford a colorless microcrystalline solid (54.7 g, 80%). Recrystallization from MeOH afforded material that displayed mp 197-201 °C (lit.[1b] mp 212 °C for pure Thiele's acid). This material, which consists primarily of Thiele's acid (**2i**) along with isomeric minor product(s),[5] was used as obtained without further purification or characterization.

Intramolecular [2 + 2] Photocyclization of "Crude Thiele's Acid". A solution of the crude Thiele's acid (**2i**, 5.00 g, 22.7 mmol, *vide supra*) in acetone (500 mL) was irradiated with a Hanovia 450 W medium pressure Hg immersion lamp for 24 h. The reaction mixture was concentrated *in vacuo*, and the residue, a pale brown solid, was dissolved in a minimum quantity of saturated aqueous $NaHCO_3$ (10 mL). Water (150 mL) was added, and the resulting aqueous solution was extracted with Et_2O (2 × 30 mL). The ethereal extracts were discarded, and the aqueous layer was rendered acidic by dropwise addition of 6 *N* aqueous H_2SO_4 until the aqueous layer became slightly cloudy. The resulting suspension was allowed to stand overnight at ambient temperature to complete precipitation of the desired product. The solid precipitate was collected by suction filtration and air dried. Crude **3a** (R = H) (180 mg, 3.6%) was thereby obtained as a colorless microcrystalline solid: mp 248 °C (dec.); IR (KBr) 3665-3050 (br, s), 2974 (s), 1699 (m), 1547 (s), 1402 (m), 1109 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.60 (*AB*, J_{AB} = 11.3 Hz, 2 H), 1.82 (*AB*, J_{AB} = 11.3 Hz, 2 H), 2.60 (m, 2 H), 2.96 (m, 4 H), 4.35 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 40.3 (t), 42.9 (d), 47.3 (d), 48.4 (d), 55.9 (s), 177.0 (s). Compound **3a** (R = H) was further characterized by conversion to the corresponding di(*p*-nitrobenzyl) ester derivative (*vide infra*).

After removal of **3a** (R = H) by filtration had been completed, the remaining filtrate was further acidified by addition of 6 *N* aqueous H_2SO_4 (15 mL, excess), whereupon additional material precipitated from solution. This material was collected by suction filtration and air-dried, thereby affording **3i** (R = H) (610 mg, 12%). Finally, the aqueous layer was extracted with Et_2O (4 × 25 mL). The combined organic layers were dried

($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. An additional quantity of **3i** (R = H) [2.6 g, 52%; total yield of **3i** (R = H) collected was 64%] was thereby obtained. Recrystallization of this material from Et_2O-pentane mixed solvent afforded pure **3i** (R = H): mp 198-200 °C (lit.[2] mp 206-207 °C ; IR (KBr) 3330-2527 (br, s), 1707 (s), 1425 (m), 1258 (m), 1132 (m), 946 (m), 644 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.50 (*AB*, J_{AB} = 5.8 Hz, 1 H), 1.68 (t, *J* = 5.8 Hz, 2 H), 2.16 (*AB*, J_{AB} = 5.8 Hz, 1 H), 2.57 (m, 1 H), 2.72-3.02 (m, 4 H), 3.10-3.22 (m, 1 H), 11.75 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.3 (t), 38.7 (t), 40.9 (d), 41.2 (d), 43.5 (d), 43.9 (d), 47.5 (d), 54.7 (d), 59.2 (s), 61.6 (s), 180.0 (s), 180.3 (s). Anal. Calcd for $C_{12}H_{12}O_4$: C, 64.85; H, 6.35. Found: C, 64.70; H, 6.36.

Di(*p*-nitrobenzyl)pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-dicarboxylate [3a (R = *p*-nitrobenzyl)]. A mixture of **3a** (R = H) (50 mg, 0.23 mmol), $SOCl_2$ (5 mL, excess), and pyridine (5 μL) was heated with stirring at 60 °C for 0.5 h. The reaction mixture was concentrated *in vacuo* to remove excess $SOCl_2$. To the residue was added *p*-nitrobenzyl alcohol (76 mg, 0.5 mmol) in dry benzene (5 mL), and the resulting mixture was stirred at ambient temperature for 0.5 h. Benzene (10 mL) and EtOAc (10 mL) were added to dissolve all of the solid material present in the reaction mixture. The resulting solution was washed with water (10 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica by eluting with 30% EtOAc-hexane. Fractional recrystallization of the material thereby obtained from Et_2O-hexane mixed solvent afforded pure **3a** (R = *p*-nitrobenzyl) (54 mg, 49%) as a colorless microcrystalline solid: mp 122.5-123.0 °C; IR (KBr) 2986 (m), 1742 (s), 1723 (s), 1609 (m), 1526 (vs), 1283 (s), 1194 (s), 1107 (s), 1065 (s), 856 (m), 739 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.77 (*AB*, J_{AB} = 10.6 Hz, 2 H), 2.01 (*AB*, J_{AB} = 10.6 Hz, 2 H), 2.80 (m 2 H), 3.14 (m, 4 H), 5.27 (s, 4 H), 7.52 (*AB*, J_{AB} = 8.5 Hz, 4 H), 8.23 (*AB*, J_{AB} = 8.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 40.4 (t), 43.2 (d), 47.6 (d), 48.5 (d), 56.0 (s), 64.6 (t), 123.8 (d), 128.1 (d), 143.5 (s), 144.0 (s), 148.0 (s), 173.8 (s). Anal. Calcd for $C_{26}H_{22}N_2O_8$: C, 63.67; H, 4.52. Found: C, 63.45; H, 4.54. The structure of **3a** (R = *p*-nitrobenzyl) was established unequivocally by application of X-ray crystallographic methods (*vide infra*).

Esterification of "Crude Thiele's Acid". To a solution of the crude Thiele's acid prepared as described above (44 g, 0.20 mol, *vide supra*) in MeOH (600 mL) was added concentrated H_2SO_4 (35 mL), and the resulting solution was refluxed overnight. The reaction mixture was cooled to ambient temperature and then concentrated *in vacuo* to a total volume of 100 mL. Water (400 mL) was added, and the resulting mixture was neutralized by careful addition of 10% aqueous $NaHCO_3$ (*ca.* 25 mL). The resulting aqueous suspension was extracted with Et_2O (4 x 100 mL). The combined ethereal extracts were washed successively with saturated aqueous $NaHCO_3$ (50mL), 2 *N* aqueous HCl (50 mL) and brine (50 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of the residue from ligroin (bp 60-80 °C) afforded pure Thiele's ester [**2i** (R = Me), 28.6 g, 60%] as a colorless microcrystalline solid: mp 85 °C (lit.[1b,5] mp 85 °C). The ^1H NMR and ^{13}C NMR spectra of the material thereby obtained were essentially identical with previously published spectra of authentic Thiele's ester).[3]

The remaining mother liquor was concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel by eluting with 10% EtOAc-ligroin. Workup of the first chromatography fraction thereby obtained afforded a pale yellow oil (871 mg, 1.8 %). Analysis of the ^1H and ^{13}C NMR spectrum of this material indicated that it consists of two products, **A** and **B** (product ratio: **A** : **B** = *ca.* 1 : 1), that are isomeric with Thiele's ester. Further attempts to separate this mixture of products by column chromatography were not successful; IR (neat) 3067 (w), 2959 (s), 2876 (w), 1724 (s) 1632 (m), 1441 (m), 1358 (m), 1290 (m), 1240 (s), 1099 (m), 770 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.20-1.50 (m, 2 × 2 H), 1.55-1.95 (m, 2 × 1 H), 2.05-2.45 (m, 2 × 1H), 2.70-3.00 (m, 2 × 3 H), 3.20-3.40 (m, 2 × 1 H), 3.60 (s, 2 × 3 H), 3.65 (s, 2 × 3 H), 5.35-5.50 (m, 2 H), 5.80-6.00 (m, 2 H), 6.40-6.50 (m, 1 H), 6.70-6.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.5 (t), 34.0 (t), 40.7 (d), 41.1 (d), 45.4 (d), 46.2 (d), 46.3 (d), 46.9 (d), 50.1 (t), 50.4 (t), 51.05 (q), 51.14 (q), 53.1 (s, 2 C), 54.1 (d), 54.9 (d), 130.6 (d), 132.80 (d), 132.85 (d), 135.5 (d), 136.9 (s), 137.9 (s), 144.3 (d), 148.3 (d), 165.4 (s, 2 C), 165.6 (s, 2 C). HRMS Calcd for $C_{14}H_{16}O_4$: $[M_r + H]^+$ 249.11268. Found: $[M_r + H]^+$ 249.11228.

Continued elution of the chromatography column afforded a second fraction; workup of this fraction afforded pure **2n** (R = Me) (557 mg, 1.1%) as a colorless microcrystalline solid: mp 99-100 °C; UV λ_{max}(EtOH 231 (log ε 3.79); IR (KBr) 2965 (w), 1732 (s), 1717 (s), 1607 (w), 1439 (m), 1277 (s), 1161 (m), 1090 (w), 1042 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.60 (br s, 2 H), 1.75 (d, J = 15.5 Hz, 1 H), 2.35 (dd, J = 10.6, 8.3 Hz, 1 H), 3.22 (dd, J = 8.3, 3.6 Hz, 1 H), 3.30 (br m, 2 H), 3.68 (s, 6 H), 5.50 (m, 2 H), 6.82 (d, J = 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 34.5 (t), 45.8 (d), 46.7 (d), 48.9 (t), 51.2 (d), 51.4 (q), 52.2 (q), 70.1 (s), 129.8 (d), 134.8 (d), 139.5 (s), 147.8 (d), 165.5 (s), 175.7 (s); Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.55; H, 6.61.

Continued elution of the chromatography column afforded a third fraction; workup of this fraction afforded pure **2a** (R = Me, 6.04 g, 13%) as a colorless oil; UV λ_{max}(EtOH) 222 (log ε 3.69); IR (neat) 2955 (s), 1738 (s), 1723 (s), 1445 (m), 1242 (m), 764 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.55-1.80 (m, 3 H), 1.85-2.00 (m, 1 H), 2.35-2.52 (m, 1 H), 2.90-3.05 (m, 2 H), 3.65 (s, 3 H), 3.75 (s, 3 H), 6.00-6.10 (m, 2 H), 6.52-6.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.4 (t), 42.3 (d), 46.5 (d), 51.1 (q), 51.6 (q), 53.1 (t), 58.7 (d), 60.9 (s), 133.2 (d), 134.3 (d), 138.1 (s), 141.8 (d), 165.0 (s), 174.0 (s). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.60: H, 6.59.

Intramolecular [2 + 2] Photocyclization of 2a (R = Me). A solution of **2a** (R = Me) (393 mg, 1.58 mmol) in acetone (150 mL) was irradiated in a quartz immersion photolysis apparatus by using a Hanovia 450W medium pressure Hg lamp during 24 h. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in Et_2O (50 mL). The resulting solution was washed sequentially with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL) 10% aqueous HCl (20 mL), water (20 mL) and brine (20 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting with 10% EtOAc-ligroin. Pure **3a** (R = Me) (117 mg, 30%) was thereby obtained as a colorless microcrystalline solid: mp 54-55 °C; IR (neat) 2969 (s), 2866 (w), 1730 (s), 1439 (m), 1327 (m), 1292 (m), 1248 (m), 1215 (m), 1196 (m), 1111 (w), 1065 (w), 945 (w), 779 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.65 (*AB*, J_{AB} = 12.8 Hz, 2 H), 1.90 (A*B*, J_{AB} = 12.8 Hz, 2 H), 2.65 (m, 2 H), 3.00 (m, 4 H), 3.70 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 40.2 (t), 42.8 (d), 47.4 (d), 48.3 (d), 51.4 (q), 55.8 (s), 174.7 (s); Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.51; H, 6.35.

Intramolecular [2 + 2] Photocyclization of 2n (R = Me). A solution of **2n** (R = Me) (159 mg, 0.64 mmol) in acetone (150 mL) was irradiated by using the procedure described above for the corresponding intramolecular [2 + 2] photocyclization of **2a** (R = Me). The crude reaction product, obtained by using the workup procedure described above, was purified by column chromatography on silica gel by eluting with 10% EtOAc-ligroin. Pure **3n** (R = Me) (56 mg, 35%) was thereby obtained as a pale yellow oil; IR (film) 2976 (s), 2874 (w), 1723 (s) 1439 (m), 1381 (w), 1333 (m), 1279 (m), 1221 (m), 1161 (m), 1076 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.55 (*AB*, J_{AB} = 9.7 Hz, 2 H), 1.75 (A*B*, J_{AB} = 9.7 Hz, 2 H), 2.78-2.92 (m, 4 H), 3.14 (m, 2 H), 3.54 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 37.8 (t), 42.0 (d), 45.5 (d), 51.7 (q), 52.7 (d), 56.4 (s), 174.7 (s). HRMS Calcd for $C_{14}H_{16}O_4$: $[M_r + H]^+$ 249.11268. Found: $[M_r + H]^+$ 249.11256.

Intramolecular Photocyclization of a Mixture of A and B. A solution that contained a 1:1 mixture of **A** and **B** (426 mg, 0.58 mmol) in acetone (150 mL) was irradiated by using the procedure described above for the corresponding intramolecular [2 + 2] photocyclization of **2a** (R = Me). The crude reaction product, obtained by using the workup procedure described above, was purified by column chromatography on silica gel by eluting with 10% EtOAc-ligroin. A mixture of cage diesters **E** and **F** (134 mg, 31%, product ratio **E** : **F** = 2.5 : 1) was thereby obtained as a colorless oil; IR (neat) 2976 (s), 2861 (w), 1723 (s), 1435 (w), 1325 (m), 1300 (w), 1256 (w), 1211 (m), 1051 cm^{-1} (w). HRMS Calcd for $C_{14}H_{16}O_4$: $[M_r + H]^+$ 249.11268. Found: $[M_r + H]^+$ 249.11259. Compound **E** (major product): ^1H NMR ($CDCl_3$) δ 1.22 (*AB*, J_{AB} = 10.6 Hz, 1 H), 1.55 (m, 2 H), 1.82 (A*B*, J_{AB} = 10.6 Hz, 1 H), 2.38-3.00 (m, 6 H), 3.62 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 38.2 (t), 39.6 (d), 40.6 (t), 40.8 (d), 43.5 (d), 43.9 (d), 46.5 (d), 47.8 (q), 48.3 (q), 51.3 (d), 56.2 (2C, s), 175.7 (2C, s); Compound **F** (minor product): ^1H NMR ($CDCl_3$) δ 1.40 (*AB*, J_{AB} =11.7 Hz, 1 H), 1.55 (m, 2 H), 1.72 (A*B*, J_{AB} =11.7 Hz, 1 H), 2.38-3.00 (m, 6

H), 3.55 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 36.8 (d), 37.8 (t), 38.2 (t, overlapped), 41.2 (d), 42.4 (d), 45.18 (d), 45.25 (d), 47.6 (d), 51.3 (d), 52.6 (d), 56.7 (s, 2 C), 175.1 (s, 2 C).

X-ray Structure of Di(*p*-nitrobenzyl) Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-dicarboxylate [3a (R =*p*-nitrobenzyl)]. All data were collected at ambient temperature on a Rigaku AFC6S diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54178 Å) by using the ω–2θ scan technique with multiple scans for weak reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.50 to 1.00. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[9] and was refined and analyzed by using TEXSAN.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[11] X-ray data and processing parameters for **3a** ($C_{26}H_{22}N_2O_8$): Crystal size 0.25 x 0.20 x 0.35 mm; Space group $P2_1/n$; a = 6.208 (2) Å; b = 40.30 (2) Å; c = 9.444 (4) Å; β = 104.80°; V = 2284 (1) Å^3; Z = 4; D_{calc} = 1.426 g-cm^{-3}; μ = 9.01 cm^{-1}; T = 296 K; $2\theta_{max}$ = 157.4°; 5152 total reflections; 4755 unique reflections; 1940 observed reflections, I ≥ 3σ(I); 325 parameters, R = 0.140; R_w = 0.101; $(\Delta/\sigma)_{max}$ = 0.00; ρ_{max} = 0.45 eÅ^{-3}; ρ_{min} = 0.60 eÅ^{-3}. A structure drawing of **3a** (R = *p*-nitrobenzyl) is shown in Figure 1.

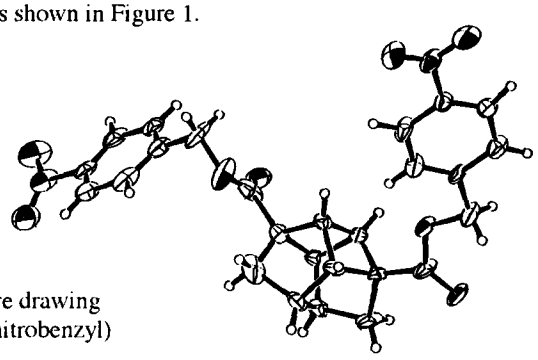


Figure 1. X-ray structure drawing of **3a** (R = *p*-nitrobenzyl)

Acknowledgement: We thank the Office of Naval Research (Grant N00014-98-1-0478, A. P. M.) and the Robert A. Welch Foundation [Grants B-0963 (A. P. M.) and P-0074 (W. H. W.)] for financial support of this study. We thank Dr. Bishwajit Ganguly for having kindly provided the AM1-calculated heats of formation of **2a** and **2n**. Finally, we thank Professor Jennifer S. Brodbelt (Department of Chemistry, University of Texas at Austin) for having kindly obtained the high-resolution chemical ionization mass spectral data reported herein.

References and Footnotes

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