Further Studies in Pentacycloundecan-8-one Photochemistry

Ronald R. Sauers* and Tyler A. Stevenson

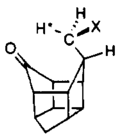
Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08904

Received July 23, 1991

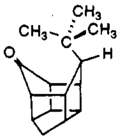
Three new *syn*-11-substituted pentacycloundecan-8-ones **1a–c** (X = CN, CO_2CH_3, C_6H_5) have been synthesized and evaluated for photochemical reactivity in the context of the development of a force field methodology for evaluation of Norrish Type II reactions. None of these compounds underwent significant intramolecular hydrogen abstraction reactions or showed evidence for interactions between the excited alkanone and the proximate methylene hydrogens. The absence of isotope effect in the fluorescence of the deuteriated analogue of **1a** provides strong evidence that there are no radiationless processes involving the proximate hydrogens that deactivate the singlet state of this ketone. A novel photostimulated interaction between alkanone singlet states and a "remote" cyano group was observed and rationalized in terms of dynamic processes during the excited state lifetime. Evidence is presented for competing long-range and contact interactions between singlet aryl rings and ground-state carbonyl groups. *syn*-11-*tert*-Butylpentacycloundecanone (**2**) was prepared and found to be photochemically unreactive as a consequence of a large increase in steric energy associated with formation of the transition structure.

Introduction

Previous studies designed to investigate the importance of stereoelectronic effects in hydrogen abstraction reactions by excited carbonyl groups, i.e., Norrish Type II reactions,[1] led to an investigation of the photochemistry of pentacycloundecan-8-ones (1). Because of the well-defined geometry of this framework, these substrates appeared to be ideally suited to reveal structural and stereochemical details of reactivity. In the first series that was studied (1, X = H, CH_3, Br, Cl), none of the compounds were photoreactive [$\phi_{-K} < 10^{-3}$] and fluorescence quantum yields were essentially independent of substituent despite the proximity of the methylenic hydrogen atoms to the carbonyl group (ground state O···H* separation ~2.6 Å). It was concluded that there was a stereoelectronic barrier to bonding interactions between the alkanone excited states and the proximate hydrogen atoms. This concept has been discussed by previous workers.[2] Turro and Weiss in 1971 suggested that good overlap between the half-filled n orbital on oxygen with the hydrogen being abstracted was an important factor.[2a] Wagner in 1976 proposed a $\cos^2$ dependency of abstraction rate vs the dihedral angle associated with the developing O–H bond and nodal plane of the carbonyl π system.[2e] A similar, but more detailed approach has been proposed by Scheffer and Trotter, et al. (see below).[2c,3] More recently, the results of semiempirical and ab initio computations[4] have provided a firm theoretical basis for the preferred angular relationships around the reaction center. Unfortunately, because it is not feasible to routinely evaluate the structures and energetics of complex systems by this methodology, an alternative methodology for quantitative analysis of these reactions is clearly desirable.



1a : X=CN
1b : X=CO_2CH_3
1c : X=C_6H_5
1d : X=CO_2H
1e : X=H



2

We have been developing a force field protocol for analysis of intramolecular hydrogen abstraction reactions in an effort to devise a quantitative computational methodology to analyze Norrish Type II photochemical reactions.[5a] The method utilizes molecular mechanics to model the structures and steric energies of excited states and the corresponding transition structures and compares the differences with those of known reactive systems, e.g. 2-pentanone. Our thesis is that by examining examples of reactive and unreactive systems, it should be possible to develop force field parameters that will correlate their reactivities and provide a basis for understanidng the interplay of the various structural factors that control these reactions. Our initial studies led to a set of parameters that indicate that hydrogen abstraction in 1 and its derivatives would proceed via strained transition states relative to 2-pentanone. Although earlier experimental tests with 1 supported this prediction, it was especially important to evaluate the reactivity of 1 more rigorously since it was to serve as a prototype of an unreactive ketone.

In this study we test further the reactivity of the methylene-X hydrogen atoms of 1 by use of substituents designed to stabilize an incipient odd electron species at this site by inductive and/or resonance effects. To this end, syntheses of the cyano derivative **1a**, the carbomethoxy system **1b**, and the benzyl system **1c** are reported. In addition, the *tert*-butyl derivative **2**, a unique example of a flagpole-substituted boat form of cyclohexanone, was designed as an alternative probe of carbonyl reactivity in this framework. Overall photoreactivity and various photophysical properties were examined for these molecules in an effort to reveal singlet-state and triplet-state hydrogen abstraction processes.[5b]

Results

Syntheses. The carbomethoxy system **1b** (X = CO_2CH_3) and the nitrile **1a** (X = CN) were prepared by the procedures of Marchand et al. starting from the known ketal **3** (eq 1).[6] The assignment of syn stereochemistry in both syntheses is based on stereochemical precedents

---

[1] Sauers, R. R.; Scimone, A.; Shams, H. *J. Org. Chem.* **1988**, *53*, 6084–6089.

[2] (a) Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1971**, *90*, 2185–2186. (b) Scheffer, J. R. in *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: New York, 1987; Chapter 1. (c) Chang, H. C.; Popovitz-Biro, R.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1978**, *109*, 3883–3893. (d) Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227–366. (e) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–52. (f) Sugiyama, N.; Nishio, T.; Yamada, K.; Aoyama, H. *Bull. Soc. Chem. Jpn.* **1970**, *43*, 1879–1880.

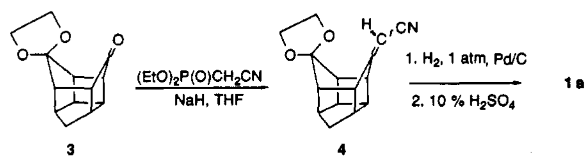
[3] Scheffer, J. R.; Trotter, J.; Omkaram, N.; Evans, S. V.; Ariel, S. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 169–196.

[4] (a) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508–7514. (b) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231–3233. (c) Severance, D.; Morrison, H. *Chem. Phys. Lett.* **1989**, *163*, 545–548. (d) Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935–4941.

[5] (a) Sauers, R. R. Krogh-Jespersen, K. *Tetrahedron Lett.* **1989**, 527–530. (b) Sauers, R. R.; Huang, S.-Y. *Tetrahedron Lett.* **1990**, 5709–5712.

[6] Marchand, A. P.; Deshpande, M. N. *J. Org. Chem.* **1989**, *54*, 3226–3229.

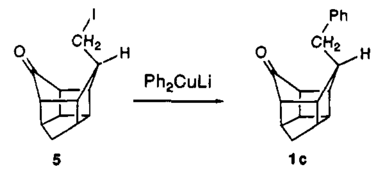
0022-3263/92/1957-0671$03.00/0



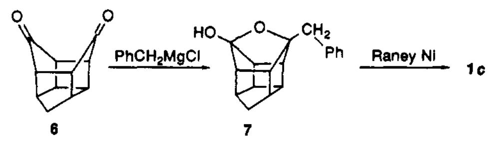
(1)

for catalytic hydrogenations in this system that have been established by these workers.

The benzyl derivative **1c** (X = C_6H_5) was prepared by two independent routes. Reaction of phenyl cuprate with the known[1] iodo compound **5** gave **1c** in poor yield (eq 2). A more reliable route involved addition of benzylmagnesium chloride to 8,11-pentacycloundecanedione followed by catalytic homodebenzylation (eq 3). In addition to the desired *syn*-benzyl ketone a small amount of an alcohol was produced that corresponded to the *anti*-benzyl system.



(2)



(3)

Synthesis of ketone **2** required a less bulky protecting group for the incipient carbonyl center. Attempts to use **3** led to neighboring group rearrangements in later stages. For this reason, the methoxymethyl **8** proved to be a more versatile substrate. A Wadsworth–Emmons carboxyvinylation reaction on **8** followed by catalytic reduction led to a 87:13 mixture of esters **9**. The major product in this sequence was assigned the syn configuration in accord with precedent for the catalytic hydrogenation step established by Marchand et al.[6] The mixture of esters was subjected to bis-methylation in two separate stages to form **10**. Upon reduction with lithium aluminum hydride the resulting mixture of neopentyl alcohols was separated by flash chromatography to yield the pure alcohol **11**, X = OH (Scheme I). The stereochemical assignment was confirmed by examination of the coupling constants for the hydrogen H-11. In all derivatives of syn isomers in this framework, this proton appears as a triplet as a result of coupling with the two vicinal protons on the adjacent five-membered ring. The major alcohol **11** (X = OH) formed in the reduction showed a 1-H triplet at δ 1.46 (J = 3.2 Hz) for this proton in the ^{1}H NMR spectrum. In the minor product (anti isomer) this absorption appeared as a singlet at δ 1.78. The neopentyl alcohol was converted to the *tert*-butyl ether **11** (X = H) via reduction of the *p*-toluenesulfonate derivative **11** (X = OTs) with Super-Hydride. The *tert*-butyl ketone **2** was smoothly generated in one stage by treatment of the methoxymethyl ether **11** (X = H) with acidic aqueous sodium dichromate.

Spectral Data. Absorption and fluorescence spectral data for the new compounds referenced to *syn*-11-methylpentacycloundecan-8-one (**1e**, R = H) are shown in Table I.

Photochemistry. Irradiations of **1a–c** and **2** at 300 nm were carried out for extended periods in acetonitrile, CD_3OD, *tert*-butyl alcohol, and acetone. Monitoring by ^{1}H NMR and thin-layer chromatography did not reveal significant accumulation of new compounds or loss of starting material. Maximum quantum yields for ketone loss were less than 3 × 10^{-3}.

Scheme I

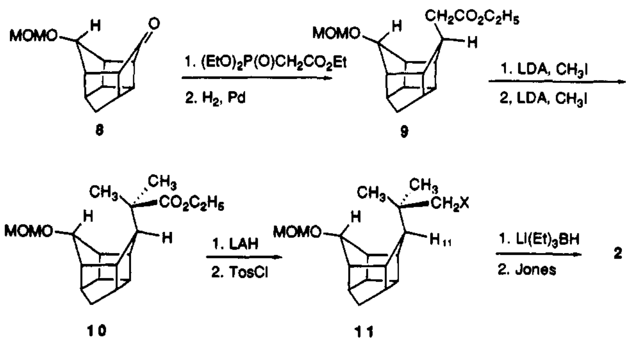


Table I. Absorption and Fluorescence Data for Ketones in Acetonitrile

	absorption		fluorescence[a]		
compd	λ_{max} (±2 nm)	ϵ_{max} (±5%)	λ_{max} (±3 nm)	ϕF_{rel} (±10%)	τ_f (ns, ±10%)
1e	296	17	441	1.00	9.6
1b	296	20	444	0.93	–
1a	299	21	439	0.23	2.3, 11
1a-d_2	–	–	439	0.22	–
1a[b]	299	17	454	0.68	2.0, 6.2
1c	298	22	440	1.02	10.5
	261	219	440	0.67[c,d]	–
2	295	26	443	0.97	6.8

[a] Excitation at 310–320 nm. [b] In cyclohexane. [c] Excitation at 262 nm. [d] Relative to **1e** at λ_{ex} 262 nm.

Discussion

The new molecules prepared in this study represent more stringent tests of the reactivity of the methylene hydrogens in **1** and its derivatives toward intramolecular hydrogen abstraction reactions. The phenyl ring in **1c** reduces the carbon–hydrogen bond strength to ca. 85 kcal/mol, for example. Similarly, the electron-withdrawing substituents, cyano and carbomethoxy, were expected to enhance reactions originating from the electron-rich π region of the excited carbonyl moiety by enhancement of the C–H acidity and/or by providing resonance stabilization of intermediate radicals.

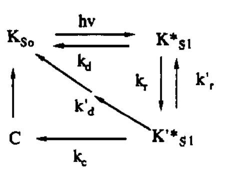
Cyano Ketone 1a. Although the cyano system (**1a**) proved to be photochemically stable, it displayed a ca. 4.5-fold reduction in fluorescence intensity relative to the methyl system. Initially, this observation was believed to be evidence for reversible hydrogen abstraction reactions between the carbonyl singlet and the proximate hydrogen atoms. These notions were dispelled by the observation that the corresponding α-dideuterio compound showed the same reduced fluorescence yield. Evidence that partial charge transfer is involved in the interaction between the two functional groups was provided by the finding that the fluorescence yield was enhanced by a factor of ca. 3 on changing the solvent from acetonitrile to cyclohexane. These observations were surprising in view of the fact that fluorescence measurements of ketones are routinely carried out in neat acetonitrile yet no evidence of solvent/solute quenching have been reported, i.e. neither lifetimes nor quantum yields of fluorescence are significantly affected by solvent changes from acetonitrile to methanol.[7]

Single photon counting measurements on **1c** carried out in the two solvents revealed dual exponential fluorescence emission profiles: (acetonitrile) 2.3 ns (86%) and 11.0 ns

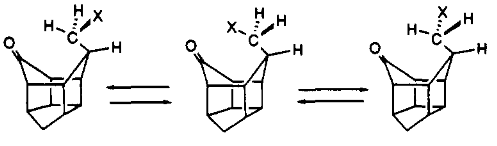
---

[7] Encinas, M. V.; Lissi, E. A.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 948–951.

Scheme II

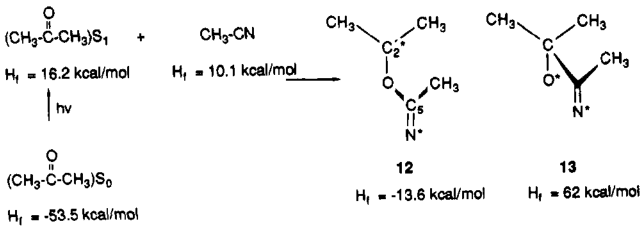


Scheme III



anti-1 *syn*-1 *anti'*-1

Scheme IV



(14%); (cyclohexane) 2.0 ns (12%) and 6.2 ns (88%). For comparison, the methyl derivative **1e** (R = H) showed a monotonic decay curve with τ = 9.6 ns in acetonitrile. A deceptively simple interpretation (Scheme II) of the data would suggest that the carbonyl group in **1a** exists in two distinct environments: "normal" conformations K* that give rise to the longer lived emission, and a conformation K′* in which carbonyl:cyano interaction (k_c) competes with emission and intersystem crossing (k'_d).

Dual fluorescence behavior is expected under two sets of conditions.[8] On the one hand, if significant fractions of the conformers are "locked" into specific rotamers, i.e., single bond rotational rates are slower than carbonyl decay rates (k_r, $k'_r \ll k_d$, k_c, and k'_d), individual conformers will fluoresce independently giving rise to two discrete τ values. Analysis of the energetics this system by molecular mechanics dispels this possibility. The three possible conformers of **1a** are depicted in Scheme III (X = CN). The two anti forms of the cyano compound have steric energies of 70.5 kcal/mol, but a minimum-energy conformation for the syn conformer was not located. A major destabilizing feature of this form is the repulsive electrostatic interaction between the carbonyl and cyano dipoles. The steric energy of the rotationally "fixed" syn conformer was ~77 kcal/mol, and all attempts to find minima near this geometry failed. Consequently, the ground-state conformational population consists of anti conformers to a large extent. Because excitation would give rise exclusively to anti excited states, only one fluorescence lifetime would be expected given the above conditions (k_r, $k'_r \ll k_d$, k_c, and k'_d) and assuming that the two anti forms have similar lifetimes and fluorescence rates.

At the other extreme where k_r, $k'_r \gg k_d$, k_c, and k'_d, a single exponential fluorescence decay curve is expected because conformational equilibration is estblished and maintained before decay. By default, the best representation of the case at hand lies between these extremes and is described by eqs 4 and 5 in which I_{syn} and I_{anti}

$$I_{\text{syn}} = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} \quad (4)$$

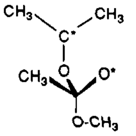
$$I_{\text{anti}} = \beta_1 e^{-t/\tau_1} + \beta_2 e^{-t/\tau_2} \quad (5)$$

represent the time dependence of fluorescence intensity from the syn and (combined) anti sites. The experimentally determined "lifetimes" τ_1 and τ_2 represent *composites* of the rate constants for conformational interconversions and decay modes of the excited states in question.[9] Thus, k_c and conformational interconversion rates are of the same order of magnitude as the typical singlet alkanone decay rate for these systems, i.e. ~10^8 s^{-1}.

Insight into the nature of the singlet carbonyl:nitrile interaction was gained by use of semiempirical methodology to examine energies and geometries of model systems. Initial calculations were done on acetonitrile and acetone (S_1) using the AM1 Hamiltonian.[10] Because the HOMO–LUMO gap for this system is fairly small (ca. 5.0 eV) and the LUMO orbital is associated with the π bond of the cyano group, we investigated the possibility that biradicals analogous to **12** might be involved in the radiationless decay of alkanone singlet states. An energy/geometry minimized structure for this intermediate was not obtained using AM1. Instead, the energy-gradient profile showed a sharp discontinuity at which point the adduct fragmented into its ground-state components. Repetition of the calculations for **12** using MINDO/3 Hamiltonian[11] gave rise to a true minimum-energy structure. Comparison of the heats of formation for acetone singlet and acetonitrile with those of intermediate **12** is shown in Scheme IV and provides support for the contention that formation of **12** could provide a viable pathway for radiationless decay. The isomeric species **13** was not considered further in view of its high energy.

Regardless of the nature of the intramolecular quenching mechanism in **1c**, it is of interest to speculate on the lack of intermolecular quenching of alkanone singlet states by bulk acetonitrile (18.9 M). Apparently $k_{c(\text{inter})}[CH_3CN]$ is considerably less than 10^8 s^{-1} (typical alkanone singlet-state decay rate) which would lead to a value of $k_{c(\text{inter})} \ll 5 \times 10^6$ M^{-1} s^{-1}. This finding is consistent with our estimate of the intramolecular rate of quenching (~10^8 s^{-1}) since rate enhancements of 10^3–10^5 are commonly found for intramolecular vs intermolecular processes.

Carbomethoxy Ketone 1b. This compound was also unreactive on long irradiation, and the fluorescence efficiency is unaffected by the presence of the carboxy group. In view of the similarity in the polar nature of carboxy groups and cyano groups it was important to compare the analogous interactions between excited singlet carbonyl groups and the CO_2R moiety. A stable complex, i.e. biradical **14**, could not be found for using MINDO/3 Hamiltonian. Instead, this structure fragmented during the energy minimization computation routine to produce ground-state acetone and methyl acetate.



14

Benzyl Ketone 1c. The benzyl ketone (**1c**) was essentially inert under irradiation conditions (310 nm) ex-

---

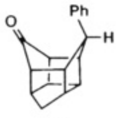
[8] For a general discussion of conformation dependent photochemistry, see: Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461–467.

[9] (a) Lakowicz, J. R. Principles of Spectroscopy, Plenum, New York, 1986, Chap. 3. (b) Laws, W. R.; Brand, L. *J. Phys. Chem.* **1979**, *83*, 795–810.

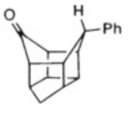
[10] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P., *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

[11] Bingham, R. C.; Dewar, M. J. S.; Ho, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1302–1306.

pected to reveal singlet-state and triplet-state reactions (acetone and alcoholic solvents). In addition, the fluorescence behavior of this ketone (cf. Table I) gave no indication of carbonyl singlet:H–C interaction. Irradiation into the phenyl chromophore (262 nm) resulted in fluorescence solely from the carbonyl group but in reduced (~66%) efficiency compared to irradiation into the carbonyl group. This result contrasts with the behavior of the related *syn*- and *anti*-11-phenylpentacycloundecanones[12] (**15s, 15a**) both of which are believed to



15s



15a

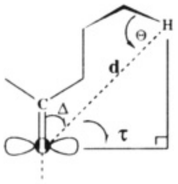
undergo complete $S_1(Ar)–S_1(K)$ energy transfer under similar conditions. The rate of energy transfer was estimated to be $\gg 10^9\ s^{-1}$ in these systems, since neither fluorescence ($k_f \sim 10^6\ s^{-1}$) nor intersystem crossing ($k_{ST} \sim 10^7\ s^{-1}$) competed successfully with energy transfer. In **1c**, the lifetime of the aryl singlet state must also be short ($<10^9\ s^{-1}$) because no aryl fluorescence was observed. Since about one-third of the aryl singlets do not transfer energy, some other radiationless decay process must be operative. Molecular mechanics calculations showed that the ground-state conformer population again consists overwhelmingly of the anti conformers. All three conformations of the phenyl group lead to stable minima (Scheme III, X = Ph): syn (steric energy = 85.2 kcal/mol), and two anti conformers (steric energy = 80.2 kcal/mol).

The behavior of the benzyl ketone can be rationalized by consideration of the competition between two physical models for interaction between the two chromophores: long range and contact.[12] Upon excitation at 262 nm, the anti excited aryl group ($K^*_{S_1}$ in Scheme II) produced first undergoes long-range electronic energy transfer (by analogy with **15a**) in competition with anti–syn interconversion to form $K'^*_{S_1}$. Singlet aryl groups that reach the syn conformation can decay nonradiatively by contact coupling (CO_{HOMO}:Ar_{LUMO}). Rates of single-bond rotation and coupling would necessarily comparable to the expected rate of intramolecular $S_1(Ar)–S_1(K)$ energy transfer ($10^9\ s^{-1}$). This novel separation of contact coupling and $S_1(Ar)–S_1(K)$ energy-transfer processes has not been proposed previously and may be unique to systems of this kind.

***tert*-Butyl Ketone 2.** Neither the singlet state or the triplet state of the *syn-tert*-butyl ketone **2** displayed significant photoreactivity. The measured singlet-state lifetime for **2** proved to be somewhat shorter than **1e**, but this appears to be a consequence of enhancement of the fluorescence rate constant. The calculated ratio of the two k_fs determined from the ratios of fluorescence yields and τ_f values (0.73) compares closely with the ratio of carbonyl extinction coefficients for the two compounds (0.65):

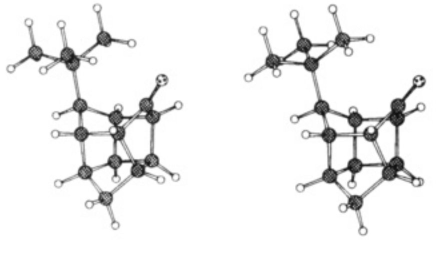
$$\frac{k^{1e}{}_f}{k^2{}_f} = \frac{\Phi_f{}^{1e}/\tau_f{}^{1e}}{\Phi_f^2/\tau_f^2} = \frac{\epsilon^{1e}}{\epsilon^2}$$

At this juncture the behavior of **2** was examined by the protocol developed by Scheffer, Trotter, et al. for analysis of intramolecular hydrogen abstraction reactions.[3] This analysis focuses on the importance of deviations of ground state geometric parameters from "ideal" parameters: *d*, Δ, Θ, and τ. It is clear from the examples cited that successful hydrogen abstractions endure significant deviations from ideal geometry as shown by the values listed below in the column headed REAL.



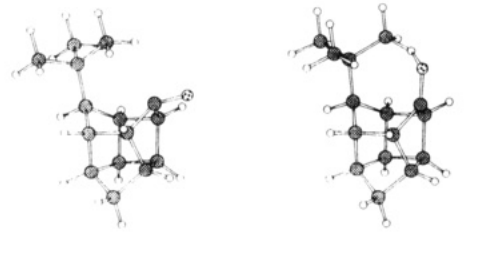
	IDEAL	REAL	KETONE **2S**	KETONE **2E**
d	2.6-3.1 Å	2.2-3.1Å	2.56 Å	2.57 Å
τ	0°	0-62°	75°	61°
Δ	90°	74-102°	79°	80°
Θ	180°	99-122°	105°	141°

The ground state of **2** was simulated by molecular mechanics calculations. The lowest energy ground-state conformation **2E** has the *tert*-butyl group in an eclipsed array with regard to the attached ring system. A slightly higher energy form **2S** was located in which the *tert*-butyl group is staggered relative to the attached bonds. Both forms show significant displacement of the carbonyl group from planarity (4.2° for **2E**; 6.7° for **2S**) as a consequence of severe steric crowding. It is likely this distortion removes some of the forbiddenness of the n-π* transition, the result of which leads to the enhanced fluorescence rate and coefficient of absorption mentioned above. Comparison of the appropriate distances and angles calculated for the two low-energy forms of ketone **2** with those of REAL examples of successful hydrogen abstractions leads to the conclusion that these criteria do not provide a sound basis for describing the lack of reactivity of **2**.



2E: Steric Energy =78.5 kcal/mol **2S:** Steric Energy =78.6 kcal/mol

Since alkanone *excited* states are known to be nonplanar and have lengthened C–O bonds,[4] a more appropriate analysis should take into account these structural differences. Two minimum-energy syn conformers (steric energy = 74.8 and 74.2 kcal/mol) and an anti conformer **2AT** (steric energy = 71.4 kcal/mol) have been generated for **2** by force field methodology developed to model ab initio derived geometries of triplet states of alkanones.[5a,13,14] The minimum change in steric energy required to reach the transition structures was evaluated by comparison of differences in steric energy of **2AT** and the transition structures derived therefrom.[15] Steric energies of the two



Steric Energy: 2AT: 71.4 kcal/mol 2ATS: 79.0 kcal/mol

transition structures derived from **2AT** by initial bonding

---

[12] For a discussion and references, see Casal, H. L.; McGimpsey, W. G.; Scaiano, J. C.; Bliss, R. A.; Sauers, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 8255–8259 (refs 2–5, 11–13, 15–19).

[13] New parameters are given in the Experimental Section.

[14] For recent evidence for puckered forms of triplet states of chair cyclohexanone, see: Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1990**, *94*, 4425–4431.

[15] Dorigo, A. E.; Houk, K. N. *J. Org. Chem.* **1988**, *53*, 1650–1664.

at the two different proximate hydrogen atoms were 79.0 (**2ATS**) and 80.7 kcal/mol. The large increase in steric energy, ~8 kcal/mol, generated during the formation of the transition structures is consistent with the lack of reactivity of **2**.[5a] A major contributing factor to the steric energy is associated with torsional strain about the Cα—C=O···H* grouping as evidenced by its sensitivity to the torsional parameter (V2) used to define this energy.[5a] In other words, when no restrictions are imposed vis-a-vis this torsion, the total steric energy is significantly reduced.

Summary and Conclusions

The above results support our contention that derivatives of **1** are unreactive for stereoelectronic reasons and are consistent with the force field protocol being developed to analyze Norrish Type II reactions. Work in pogress is designed to test these ideas more quantitatively and to provide more examples of reactions that are controlled by stereoelectronic effects. In this way, it will be possible to more narrowly define the individual parameters used in these analyses and, hence, sharpen the utility of the methodology.

Experimental Section

General Procedures. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratories, Madison, NJ. Infrared spectra were obtained on a Perkin-Elmer Model 727b spectrometer or a Mattson Cygnus 100 spectrometer. Proton NMR spectra were performed on either a Varian VXR-200 or VXR-400 spectrometer. Unless otherwise noted, the solvent was $CDCl_3$ which was also used as the internal standard. Integration data (±10%) were consistent with the assigned structures. Carbon NMR spectra were performed on the Varian VXR-200 spectrometer. Absorption spectra were obtained on either a Cary Model 17D spectrometer,a Perkin-Elmer Model 559 spectrometer, or a Hewlett-Packard Model 8450A diode array spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer Model MPF-3L spectrophotometer and acquired on a Tektronix 4052 computer. Fluorescence quantum yields (±10%) were determined relative to ketone **1e**[1] and were measured either with the aid of an integration program or by the cut and weigh technique where application of the program was not practical. Because the curves all had essentially identical band shapes, no corrections were applied. Fluorescence lifetimes were determined by time-correlated single-photon counting with a PRA instrument interfaced to an IBM XT Personal Computer equipped with deconvolution programs. Absorption and fluorescence spectroscopy were performed in either HPLC grade acetonitrile or Fisher "Spectranalyzed" cyclohexane. Irradiations were carried out in 5-mm Pyrex NMR tubes in a Rayonet Reactor equipped with 300-nm bulbs. All solutions were thoroughly deaerated with nitrogen before irradiation. Standard workup procedure involved quenching with water, multiple extractions with ether or methylene chloride, drying over $MgSO_4$ followed by evaporation, and flash chromatography using mixtures of ethyl acetate and hexanes.

Photolyses. (a) The maximum quantum yields of disappearance of ketones were estimated by calibration of the source against the Type II photocleavage of butyrophenone in benzene (ϕ_{II} = 0.33[16]). For example, with **1c** the optical density of the solutions were matched (OD = 10) and the deaerated solutions were irradiated in a Rayonet Reactor using a merry-go-round apparatus, 300-nm bulbs, and a Pyrex filter. The butyrophenone solution was irradiated 1 min/h that the **1c** solution was irradiated and conversion was kept below 6%. No change in the **1c** solution was observed after 404 min (^1H NMR). Assuming disappearance of **1c** was <1%, the quantum yield for loss of **1c** was found to have an upper limit of 0.003.

(**b**) Other irradiations were carried in a similar manner in deaerated solvents: **1a** (36 h, AcCN); **1b** (36 h, t-BuOH); **2** (t-BuOD, 7 d; AcCN, 3 d); **1c** (AcCN, 20 h; CD_3OD, 23 h). Neither ^1H NMR nor thin-layer chromatographic analysis revealed formation of any new products in any of these experiments.

8-Oxo-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneacetic Acid Methyl Ester (1b). The keto acid **1d**[6] (1.05 g, 4.82 mmol) was dissolved in 10 mL of $SOCl_2$, and the solution was refluxed for 45 min. After cooling to room temperature, a portion of methylene chloride was added and the volatiles were removed under reduced pressure. The process was repeated to yield 1.21 g of the acid chloride as a brown oil (with some unevaporated $SOCl_2$). Acid chloride formation was judged complete by disappearance of the IR band at 5.84 μm and appearance of a new IR band (film) at 5.56 mm. The acid chloride was dissolved in 30 mL of HPLC-grade MeOH. The solution was stirred overnight, and the solvent was removed under reduced pressure to yield 2.05 g of yellow solid. The yellow solid was purified by flash chromatography to yield 0.380 g (34%) of the desired keto methyl ester **1b** as a clear oil: IR (film) 5.76 μm; UV λ_{max} 296 nm (ε 20); ^1H NMR δ 1.46 (AB, J_{AB} = 10.9 Hz, 1 H), 1.84 (AB, J_{AB} = 10.9 Hz, 1 H), 2.08–2.22 (m, 1 H), 2.28–2.83 (m, 8 H), 2.96 (m, 2 H), 3.61 (s, 3 H). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.55; H, 7.06. A sample was purified for fluorescence spectroscopy by molecular distillation; bp 89–94 °C (0.05 Torr).

11-(Cyanomethylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one Ethylene Ketal (4). An oil dispersion of NaH (61.14%, 264 mg, 6.72 mmol) was charged to a flask, and to this was added 10 mL of dry THF via a syringe. The stirred suspension was cooled to 0–5 °C under nitrogen and diethyl (cyanomethyl)phosphonate (1.09 mL, 1.19 g, 6.72 mmol) was added via a syringe through the top of the condenser followed by a rinse of a few milliliters of THF. The homogeneous solution was stirred at 0 °C for 1 h. The monoprotected dione **3**[17] (0.977 g, 4.48 mmol) in 10 mL of dry THF was added dropwise via a syringe through the top of the condenser. The solution was refluxed with stirring for 2 h. The mixture was allowed to cool to 25 °C and was quenched with saturated NH_4Cl. Removal of the ether extracts in vacuo to yield 1.411 g of crude product which on purification yielded 1.028 g (95%) of the cyano compound **4** as a mixture of cis/trans isomers: IR (Nujol) 4.55 μm; ^1H NMR δ 1.42 (AB, J_{AB} = 10.8 Hz, 1 H), 1.70–1.87 (m, 1 H), 2.21–3.42 (m, 8 H), 3.68–3.97 (m, 4 H), 4.95 and 5.03 (2 s, total 1 H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.43; H, 6.17; N, 5.82.

***syn*-11-(Cyanomethyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one Ethylene Ketal.** The ketal **4** (0.945 g, 3.92 mmol) was dissolved in ca. 50 mL of ethyl acetate, and to this solution was added ca. 60 mg of 10% Pd/C. The slurry was stirred under hydrogen at atmospheric pressure for 5 days, during which time fresh catalyst was added periodically in ca. 50-mg portions for an additional total of 150 mg. The mixture was filtered over a bed of Celite, and the solvent was removed under reduced pressure to yield 1.018 g of yellow oil which was flash chromatographed to yield 0.865 g (91%) of the pure syn-saturated cyano compound as a clear oil: IR (film) 4.55 μm; ^1H NMR (400 MHz) δ 1.16 (AB, J_{AB} = 10.8 Hz, 1 H), 1.63 (AB, J_{AB} = 10.8 Hz, 1 H), 1.85 (m, 1 H), 2.07 (m, 1 H), 2.30–2.79 (m, 7 H), 3.09 (m, 2 H), 3.70–3.83 (m, 2 H), 3.94 (m, 2 H). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.31; H, 6.96; N, 5.92.

8-Oxo-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneacetonitrile (1a). The saturated cyano ketal (0.790 g, 3.25 mmol) was dissolved in 20 mL dioxane and cooled in an ice bath and treated with 10 mL of 10% H_2SO_4. The solution was stirred at room temperature for 5 d, after which time ether and water were added. After workup there was obtained 0.612 g of a yellow oil which was flash chromatographed to yield 0.527 g (81%) of the keto cyano compound **1a**. The oil crystallized to a white solid after several days at −20 °C; mp 32–33 °C; IR (film) 4.45, 5.78 μm; UV λ_{max} (CH_3CN) 299 nm (ε 21), λ_{max} (cyclohexane) 299 nm (ε 17); ^1H NMR (400 MHz) δ 1.50 (AB, J_{AB} = 11.2 Hz, 1 H), 1.87 (AB, J_{AB} = 11.2 Hz, 1 H), 2.10 (m, 1 H), 2.34–2.87 (m, 8 H), 3.03 (m, 2 H). Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.24; H, 6.71; N, 7.02.

8-Oxo-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneacetonitrile-*d*$_2$ (1a-*d*$_2$). A solution of 54 mg (0.22 mmol) of *syn*-11-(cyanomethyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one

---

[16] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177.

[17] Eaton, P. E.; Cassar, L.; Hudson, R. A.; Hwang, D. R. *J. Org. Chem.* **1976**, *41*, 1445–1448.

ethylene ketal in 18 mL of DMSO-d_6 was added to a freshly prepared solution of $NaOCD_3$ in CD_3OD (9 mg, 0.4 mmol Na reacted with 0.75 mL, 18.5 mmol CD_3OD). The solution was stirred at 25 °C for 2 d, after which most of the DMSO was distilled off at 1 Torr and 45 °C. Portions of D_2O and benzene were added, and the layers were separated to yield 50 mg (93%) of the deuterated compound after workup (the 2 H multiplet at δ 3.09 in the ^{1}H NMR spectrum was absent and the 1 H multiplet at δ 1.85 appeared as a broad singlet). The oil as subjected to deketalization conditions as above to yield 33 mg (82%) of pure **1a**-d_2: ^{1}H NMR δ 1.50 (AB, J_{AB} = 11.2 Hz, 1 H), 1.87 (AB, J_{AB} = 11.2 Hz, 1 H), 2.10 (bs, 1 H), 2.34–2.87 (m, 6 H), 3.03 (m, 2 H). For fluorescence spectroscopy, **1a**-d_2 was further purified by molecular distillation at 60 °C and 0.075 Torr followed by gas chromatography with a silicone column at 138 °C.

***anti*-11-(Methoxymethoxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (8).** A solution of 2.58 g (0.0147 mol) of *anti*-11-hydroxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one[18] in ca. 20 mL of dry THF and 11 mL of diisopropyl ethyl amine was cooled to 0 °C, and 2.5 mL of chloromethyl methyl ether (0.034 mol) was added dropwise. The mixture was stirred overnight at room temperature after which time the reaction mixture was cooled to 0 °C and another 1 mL (0.013 mol) of $ClCH_2OCH_3$ was added along with 2 mL of amine. After an additional 50 h (67 h total) the reaction was worked up to yield 2.85 g (88%) of the protected keto alcohol. An analytical sample of was obtained by flash chromatography. The pure ketone **8** (134 mg) was recovered as a clear oil: IR (film) 5.75 μm; ^{1}H NMR δ 1.63 (AB, J_{AB} = 11.0 Hz, 1 H), 1.86 (AB, J_{AB} = 11.0 Hz, 1 H), 2.22–3.07 (m, 8 H), 3.29 (s, 3 H), 3.89 (s, 1 H), 4.55 (s, 2 H). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.03; H, 7.37.

11-(Carbethoxymethylene)-*anti*-8-(methoxymethoxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane. A stirred slurry of 0.715 g of NaH (61.14% oil dispersion, 18.2 mmol) and 20 mL of dry THF was cooled to 0 °C, and triethyl phosphonoacetate (4.08 g, 18.2 mmol) was added dropwise. The homogeneous solution was stirred at 0 °C for 1 h, and the ketone **8** (2.67 g, 12.1 mmol) in ca. 20 mL of dry THF was added dropwise. The solution was refluxed for 15 min, after which time the reaction was quenched with saturated NH_4Cl to yield 4.22 g of a brown oil. After flash chromatography there was obtained 2.86 g (82%) of the unsaturated ethyl ester as a cis/trans mixture; IR (film) 5.84, 5.98 μm; ^{1}H NMR δ 1.25 (t, J = 7.0 Hz, 3 H), 1.47 (AB, J_{AB} = 11.0 Hz, 1 H), 1.72–1.83 (m, 1 H), 2.34–2.93 (m, 8 H), 3.29 (s, 3 H), 3.67 (s, 1 H), 3.88–4.20 (m, 2 H), 4.54 (m, 2 H), 5.54 and 5.61 (2 s, total 1 H). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.81; H, 7.54.

***syn*/*anti*-8-(Methoxymethoxy)-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneacetic Acid Ethyl Esters (9).** A slurry of 2.72 g (9.34 mmol) of unsaturated ethyl ester, ca. 150 mL of ethyl acetate, and 200 mg of 10% Pd/C was stirred under hydrogen at atmospheric pressure and room temperature for 8 h to afford 2.61 g (96%) of **9** as a clear oil. Proton NMR showed that the recovered product was a mixture of syn and anti isomers (83/17), which were inseparable by chromatography; IR (film) 5.77 μm; ^{1}H NMR δ 1.23 (t, J = 7.2 Hz, 3 H), 1.61–1.68 (m, 1 H), 1.87–1.97 (m, 1 H), 2.23–2.70 (m, 11 H), 3.31 (s, 3 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.20 (s, 1 H), 4.56 (s, 2 H). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.11; H, 8.38.

***syn*/*anti*-8-(Methoxymethoxy)-α-methyl-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneethanoic Acid Ethyl Esters.** LDA (13 mmol) in THF (15 mL)/5.2 mL of hexane was cooled to −72 °C in an inert atmosphere. The above esters (2.61 g, 8.93 mmol) were added in 15 mL of dry THF to the LDA solution. The mixture was stirred at −72 °C for 0.5 h, at which time a solution of MeI (13.0 mmol, 1.85 g) in 5 mL of THF and 2.3 mL of freshly distilled HMPA was added. The solution was stirred at −72 °C for 10 min and then at 0 °C for 1 h. The reaction mixture was allowed to come to room temperature and quenched. Workup yielded 2.70 g (99%) of the monoalkylated esters (two sets of diastereomers) as a clear oil: IR (film) 5.78 μm; ^{1}H NMR δ 1.02–1.31 (m, 6 H), 1.48–1.69 (m, 3 H), 2.17–2.40 (m, 3 H), 2.47–2.73 (m, 6 H), 3.31 and 3.32 (2 s, total 3 H), 3.97–4.19 (m, 2 H), 4.34 (m, 1 H), 4.55 and 4.58 (2 s, total 2 H). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.89; H, 8.64.

***syn*/*anti*-8-(Methoxymethoxy)-α,α-dimethyl-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneethanoic Acid Ethyl Esters (10).** To 13 mmol of LDA in 10 mL of THF was added dropwise the monoalkylated ester (2.13 g, 6.96 mmol) in 10 mL of dry THF. The solution was stirred at −72 °C for 10 min, 0 °C for 10 min, and 25 °C for 0.5 h. To the enolate at 25 °C was added dropwise with a syringe a solution of MeI (1.44 g, 10.1 mmol) in 3 mL of THF and 1.8 mL of HMPA. The reaction mixture was stirred at room temperature for 1.5 h and was worked up to yield 2.12 g of yellow oil. After purification there was obtained 1.34 g (60%) of a mixture of syn and anti isomers of **10**: IR (film) 5.80 μm; ^{1}H NMR δ 1.01–1.31 (m, 10 H), 1.46–1.68 (m, 2 H), 2.12–2.90 (m, 8 H), 3.28 and 3.32 (2 s, total 3 H), 3.76 (s, 1 H), 3.98–4.16 (m, 2 H), 4.52 and 4.56 (2 s, total 2 H). Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.43; H, 8.84.

***syn*-8-(Methoxymethoxy)-α,α-dimethyl-*syn*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneethanol (11, X = OH).** To a slurry of 0.300 g of lithium aluminum hydride in 100 mL of anhydrous ether was added a solution of the above diastereomeric mixture (1.26 g, 3.93 mmol) in the minimum amount of ether. The mixture was stirred 0.5 h and then quenched to afford 1.09 g of a clear oil. The syn and anti isomers were separated by flash chromatography with 20% EtOAc/hexanes to yield 0.869 g (79%) of the pure syn alcohol **11** (X = OH) as a clear oil: IR (film) 2.90 μm; ^{1}H NMR δ 0.95 (s, 3 H), 1.03 (s, 3 H), 1.23 (AB, J_{AB} = 10.4 Hz, 1 H), 1.46 (t, 1 H, J = 3.2 Hz), 1.63 (AB, J_{AB} = 10.4 Hz, 1 H), 2.18 (bs, 1 H), 2.30 (m, 2 H), 2.49–2.70 (m, 5 H), 3.21 (d, J = 4.6 Hz, 2 H), 3.32 (s, 3 H), 4.17 (s, 1 H), 4.59 (s, 2 H). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 72.88; H, 9.39.

***syn*-11-*tert*-Butylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (2).** To a solution of 2.8 g (ca. 5 equiv) of TsCl in 10 mL of pyridine was added 0.812 g (2.92 mmol) of alcohol **11**, X = OH, in ca. 8 mL of pyridine, and the solution was allowed to come to room temperature overnight. After workup there was obtained 1.26 g (100%) of the tosylate **11**, X = OTS, as a yellow solid; mp 88–89 °C.

A solution of 1.14 g (2.63 mmol) of tosylate in 2.5 mL of dry THF was cooled in an ice bath and treated with 8 mL of a 1 M solution of $Li(Et)_3BH$ in THF (3 equiv).[19] The solution was stirred at room temperature for 0.5 h and refluxed an additional 4 h. Workup yielded 1.50 g of a yellow oil which was a mixture of the reduced product, alcohol, and tosylate. The mixture was separated by flash chromatography to give 0.362 g (53%) of **11**, X = H, as a clear oil, 0.014 g of unreacted tosylate **11**, X = OTS, and 0.359 g of alcohol **11** (X = OH). The recovered alcohol was recycled through the tosylation and reduction reactions two more times to give an overall yield of 0.562 g (81%) of **11**, X = H: IR (film) 3.39, 3.48 μm; ^{1}H NMR (400 MHz) δ 0.98 (s, 9 H), 1.22 (AB, J_{AB} = 10.4 Hz, 1 H), 1.40 (m, 1 H), 1.63 (AB, J_{AB} = 10.4 Hz, 1 H), 2.15 (m, 1 H), 2.27 (m, 1 H), 2.37 (m, 1 H), 2.50–2.63 (m, 4 H), 2.67 (m, 1 H), 3.32 (s, 3 H), 4.20 (s, 1 H), 4.58 (q, J = 3.2 Hz, 2 H). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.93; H, 9.98.

A solution of 0.412 g (1.57 mmol) of **11**, X = H, in 14 mL of acetone was cooled to 0 °C and treated with 14 mL of Jones reagent (7.5 g $Na_2Cr_2O_7 \cdot 2H_2O$, 5.7 mL of concentrated H_2SO_4, 30 mL of H_2O). The mixture was stirred at 0 °C for 0.5 h and then at room temperature for 3 d. After quenching and flash chromatography there was obtained 0.325 g of the ketone **2** as a white solid. The product was sublimed at 0.25 Torr and 39 °C to yield 0.309 g (91%) of pure **2** as white crystals: mp 48–49 °C; IR (film) 5.74 μm; UV λ_{max} 295 nm (ϵ 26); ^{1}H NMR δ 0.88 (s, 9 H), 1.37 (AB, J_{AB} = 10.8 Hz, 1 H), 1.51 (m, 1 H), 1.79 (AB, J_{AB} = 10.8 Hz, 1 H), 2.20–2.33 (m, 1 H), 2.38–2.56 (m, 3 H), 2.56–2.83 (m, 2 H), 2.86–3.03 (m, 2 H); ^{13}C NMR δ 31.2, 36.0, 36.7, 40.0, 42.9, 43.1, 43.7, 49.1, 50.0, 50.7, 54.1, 219.2. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.05; H, 8.92.

***syn*-11-Benzylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (1c).** (a) Phenyl cuprate was prepared from 0.380 g (2.00 mmol) of CuI in 3 mL of anhydrous ether by reaction with 2.0 M solution

---

[18] Craze, G.-A.; Watt, I. *J. Chem. Soc., Perkin Trans. 2* **1981**, 175–184.

[19] (a) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 3064–3066. (b) Holder, R. W.; Matturo, M. G. *J. Org. Chem.* **1977**, *42*, 2166–2168.

of PhLi in cyclohexane (2.2 mL, 4.4 mmol). *syn*-11-(Iodomethyl)pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one (**5**)[1] (300 mg, 1.0 mmol) was then added in 2.5 mL of anhydrous ether, and the mixture was stirred at −72 °C for 10 min, at 0 °C for 45 min, and at 25 °C for an additional 1 h. The reaction was quenched using a mixture of 40 mL of saturated NH_4Cl and 10 mL of concentrated ammonia. After workup 275 mg of a crude product from which was obtained 45 mg of **1c** was isolated by flash chromatography.

(**b**) To the Grignard reagent prepared from 2.09 g (0.0862 mol) of magnesium and benzyl chloride (9.92 mL, 0.0862 mol) in 170 mL of anhydrous ether was added a solution of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione[20] in 100 mL of dry THF. The stirred solution was refluxed 3.5 h and stirred an additional 12 h at room temperature. After workup, 6.90 g of **7** was obtained after recrystalliztion from ethyl acetate/hexanes. Pure **7** was a white solid: mp 137–139 °C; IR (film) 3.08 μm; ^{1}H NMR δ 1.40 (AB, J_{AB} = 10 Hz, 1 H), 1.77 (AB, J_{AB} = 10 Hz, 1 H), 2.36–2.82 (m, 8 H), 3.05 (s, 2 H), 3.87 (bs, 1 H), 7.12–7.39 (m, 5 H). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.81; H, 7.10.

Hemiketal **7** (0.165 g) was dissolved in ca. 3 mL of 95% EtOH and treated with a teaspoon of W-2 Raney nickel (50% in water).[21] The solution was refluxed 1.5 h and was allowd to cool to room temperature. The slurry was filtered through a short silica gel column with ethyl acetate to remove nickel and afforded 126 mg of an oil after evaporation of the solvents. The two major products were isolated by flash chromatography with 7.5% EtOAc/hexanes. The faster moving fraction was recovered as 45 mg (27%) of a white solid and was concluded to be **1c** by virtue of its having an identical ^{1}H NMR spectrum to **1c** prepared by sequence (a): mp 48–50 °C; IR (film) 5.76 μm; UV λ_{max} 261, 298 nm (ε 219, 22); ^{1}H NMR δ 1.42 (AB, J_{AB} = 10 Hz, 1 H), 1.79 (AB, J_{AB} = 10 Hz, 1 H), 1.97 (m, 1 H), 2.35 (m, 1 H), 2.45–2.97 (m, 9 H), 7.03–7.32 (m, 5 H). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.26; H, 7.22. The sample used for fluorescence measurements was further purified by flash chromatography once with 7.5% EtOAc/hexanes and twice with 2.5% EtOAc/benzene.

***anti*-11-Benzylpentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one.** The slower moving fraction (27 mg) from the above workup was shown by IR to be an alcohol (film, 3.03 μm). A 17-mg sample of the alcohol in ca. 1 mL of acetone was oxidized with 1 mL of Jones reagent (7.5 g $Na_2Cr_2O_7{\cdot}2H_2O$, 5.7 mL of H_2SO_4, 30 mL of H_2O) to yield 26 mg of yellow oil whose R_f was identical to that of **1c**. The oil was purified by flash chromatography to afford 18 mg of a white solid, presumably the *anti*-benzyl ketone; mp 111–112 °C; IR (film) 5.77 μm; ^{1}H NMR δ 1.60 (AB, J_{AB} = 10 Hz, 1 H), 1.83 (AB, J_{AB} = 10 Hz, 1 H), 1.99 (t, 1 H), 2.18–3.10 (m, 10 H), 7.00–7.33 (m, 5 H). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 85.99; H, 7.34.

Computations. (a) Molecular Mechanics. Input coordinates were generated with MODEL, v. 2.96.[22] MM2(87) parameters were used except where noted. Carbonyl triplet-state geometry and steric energy were calculated using standard saturated oxygen parameters (no lone pairs) with the following changes: C_{sp^3}–C_{sp^3}–O_{sp^3} [k_θ = 0.700, Θ_0 = 119.00°]; O_{sp^3} [r^* = 1.35 Å, ε = 0.050 kcal/mol]. The second torsional term (V2) used for calculation of steric energy about the Cα—C—O···H* grouping was 7.5 kcal/mol. Severely crowded hydrogen atoms near the oxygen atom (O···H < 2.1 Å) use the following van der Waals constants: r* = 1.35 Å (ε = 0.047 kcal/mol).[23] These parameters replace the original set that was developed for modeling the ab initio calculated structures in ref 5a. Better correlations among the four target structures are now obtained (average deviation ~1°) and no other new parameters need to be introduced.

(**b**) **Semiempirical.** All calculations were done on a MicroVaxII using MOPAC v. 5.0.[24] Energy minimizations were fully optimized using the keywords PRECISE, BIRADICAL, and SINGLET. Further evidence for the validity of the minimum-energy structure **12** was provided by a normal coordinate analysis using the FORCE option. Positive frequencies were found for all molecular vibrations. The following select data were calculated for **12**: ionization potential, 2.98 eV; net atomic charges; O (−0.4203), C_2 (0.2563), C_5 (0.4138), N (−0.1894); dipole moment, 3.070 d; bond distances, C=N (1.249 Å), O–C_5 (1.397 Å); torsion angle C_2–O–C_5–N, −177°.

Acknowledgment. We are grateful to Dr. Chang-He Xiao for assistance with the single photon counting experiments and to Dr. A. Naughton for assistance with NMR spectra. We thank Dr. A. Scimone for preliminary data on the preparation of the benzyl system. We are also indebted to Prof. K. Krogh-Jespersen for advice on the semiempirical calculations. We thank Prof. K. Steliou for assistance with installation and operation of the molecular modeling program MODEL and Prof. A. Marchand for prepublication information.

---

(20) Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974**, *39*, 1596.

(21) (a) Bonner, W. A. *J. Am. Chem. Soc.* **1960**, *82*, 1382–1385. (b) Sauers, R. R.; Schinski, W.; Mason, M. M.; O'Hara, E.; Byrne, B. *J. Org. Chem.* **1973**, *38*, 642–646.

(22) Obtained from Dr. K. Steliou, Dept. of Chemistry, Universite de Montreal, Montreal, Quebec, Canada H3C 3V1.

(23) (a) Jaime, C.; Ōsawa, E. *Tetrahedron* **1983**, *39*, 2769–2778. (b) Ermer, O.; Mason, S.; Anet, F. A. L.; Miura, S. S. *J. Am. Chem. Soc.* **1985**, *107*, 2330–2334.

(24) Obtained from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47405.