tivity by a group 5 metal is unprecedented and further study of this and related reactions is underway.

Under comparable conditions diphenylacetylene (tolane) reacts stoichiometrically to give mononuclear complexes of composition $TaCl_3L_2$(tolane), where L represents a neutral donor such as tetrahydrothiophene (THT), tetrahydrofuran (THF), CH_3CN, or pyridine. When $TaCl_3(THT)_2$(tolane) was dissolved in acetone containing some water, hydrous Ta_2O_5 precipitated within minutes and cis-stilbene was detected in the acetone. This suggests that the attachment of the tolane to the Ta is in the nature of an oxidative addition. In this respect the product would be similar to some isoelectronic Mo(IV) species obtained by addition of alkynes to $(R_2NCS_2)_2MoO$, some of which have been compared to the active site in nitrogenase.[7,8]

We have obtained crystals of a derived compound, 4, with the formula $(pyH)[TaCl_4(py)(tolane)]$[9] and determined its structure by X-ray crystallography.[10] The anion is shown in Figure 1. The binding of the tolane to the tantalum is very strong and symmetrical. The Ta–C distances are 2.066 (8) and 2.069 (8) Å, the C–C distance is 1.325 (12) Å, and the two C(phenyl)CC angles are 138.24 (80) and 141.16 (82)°. The Ta–C distances are only slightly longer than the average for the C=Ta double bonds found in several tantalum alkylidene compounds,[11] namely, 2.04 Å, and thus a simple μ-bond representation, 5, or one with two single bonds, 6, does not seem

5   6   7
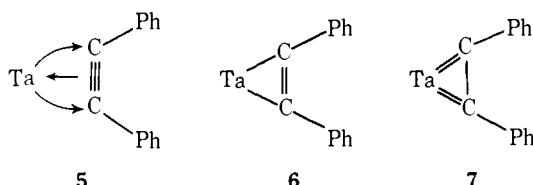
adequately to account for the structure. We therefore suggest 7 which has C=Ta double bonds and is a kind of dialkylidene. Perhaps, in resonance terms, a mixture of 6 and 7, with an appreciable contribution from 7 would best accommodate all of the chemical and structural evidence. The bond lengths and angles that occur in a compound[12] with arrangement 8 make

8
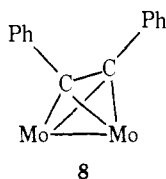
a useful comparison. Here each acetylenic carbon atom is forming two single bonds to metal atoms. Thus, we might expect the C–C distance to be similar to that in the present case, and it is, 1.329 (6) Å. On the other hand, the C–Mo distances should be much longer than our C–Ta distances, and they are, averaging 2.18 ± 0.02 Å. The Ta–C distances here are similar to those in the benzyne complex $Ta(\eta^5\text{-}C_5Me_5)(CH_3)_2$-$(C_6H_4)$[13] but very much shorter than those in $[\eta^5\text{-}C_5H_5]_2$-$Nb(O_2CCH_3)$(tolane).[14]

Comparison with the recently reported work of Weiss et al.[15] is especially pertinent. They find a W(HCCH) unit with W–C distances of 2.03 Å and a C–C distance of 1.29 Å and on the basis of these facts and other reasoning propose that the acetylene is acting as a four-electron donor. In their case this, allows the metal to achieve an 18-electron configuration, whereas for our compound Ta reaches only a 16-electron configuration. However, this is not unusual for group 5 metals.[16]

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(10) The compound crystallized in the space group $P\bar{1}$ with a = 11.375 (8), b = 12.335 (5), c = 9.352 (4) Å; α = 101.12 (3), β = 106.82 (4), γ = 87.07 (4)°; V = 1232.5 (1.0) Å^3; and Z = 2. Data were collected for $0° < 2\theta < 45°$, and 3340 reflections were found to be greater than 3σ. Least-squares refinement has yielded final discrepancy indices of R_1 = 0.031 and R_2 = 0.051. Methods of data collection and structure refinement have been described previously.[2] Tables of atomic positional and thermal parameters is available as supplementary material. See paragraph at the end of paper regarding supplementary material.
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The Importance of Hyperconjugation in Nucleophilic Vinylic Substitution

Sir:

Nucleophilic vinylic substitution via addition–elimination[1,2] (eq 1: LG = leaving group, Nu = nucleophile, Y,Y′ = activating groups) proceeds via an intermediate carbanion as indicated by the "element effect"[1-3] and by base catalysis found in several substitutions by amines.[3,4] The substitution of a good leaving group, e.g., Cl, Br, proceeds in most cases exclusively or predominantly with retention.[1,2] "Convergence",[2] i.e., approach to a similar product composition starting from either of the two isomers, is sometimes found when LG = F,[5] but mostly results from postisomerization of retained products.[1a] Two mechanisms were proposed to explain the observed retention: (a) a concerted bond formation and cleavage,[6] which was recently criticized for neglecting the other evidence above;[2] (b) formation of a planar carbanion where LG expulsion (F excluded) is faster than internal rotation, and a 60° rotation which gives retention is preferred over 120° rotation which gives inversion.[1] A related explanation was given for tetrahedral carbanions.[2] The source of the rotational barrier and the reason for the preference of a 60° rotation are not fully un-


1

(1)
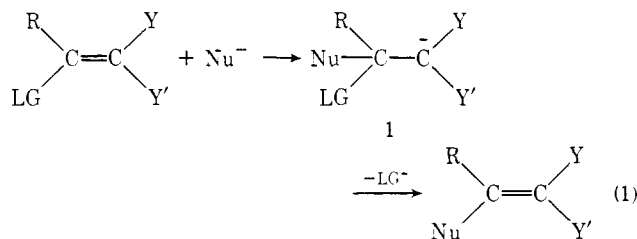
Scheme I
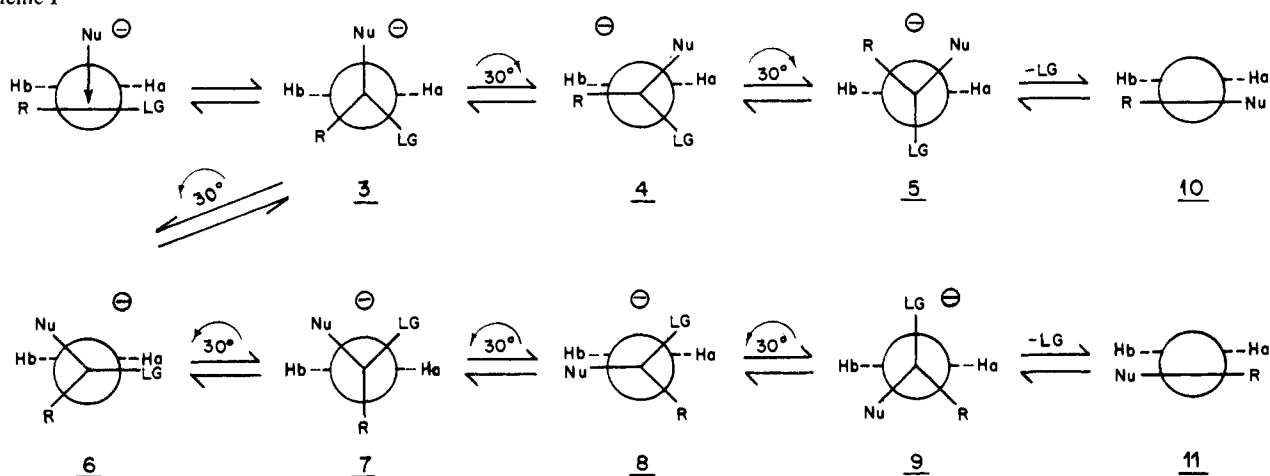
derstood. We present here MO calculations which suggest that hyperconjugation between the β substituents and the carbanionic electron pair in **1** account for these phenomena.

Reliable experimental data regarding the conformational preferences of carbanions is absent, whereas the use of neutral isoelectronic species (e.g., amines) as models for **1**[2] is questionable. We have therefore studied by ab initio methods[7] the β-substituted ethyl anions **2**,[8] in two conformations, **2a** and **2b**. The calculated total energies of **2a** and the barriers to internal rotation $E(\mathbf{2b}) - E(\mathbf{2a})$ are presented in Table I.[8b] It was
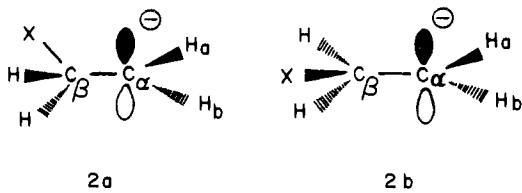
shown recently that the relative energies of anions can be reproduced accurately even with the minimal STO-3G basis set[9] used here.[10,11]

The impressively large barriers that we find are much higher than those in the analogous amines excluding their use as models for **1**. The strong conformational preferences in **2** have been ascribed to hyperconjugation (HC).[12] The hyperconjugative ability (HCA) of X is the net result of the destabilizing interaction of the occupied anionic 2p orbital on C_α and the filled σ_{C-X} orbital and the stabilizing interaction of $C^-(2p)$ with the σ^*_{C-X} orbital. HC is at a maximum in **2a** and zero in **2b** where the interacting orbitals are perpendicular. The barriers to internal rotation in **2**, which decrease in the order Cl $\gg$ OCH$_3$ $\sim$ OH $>$ F $\sim$ SH $>$ CN $\sim$ CF$_3$ $>$ NH$_2$ $\sim$ PH$_2$ $>$ CH$_3$ $>$ H $\sim$ SiH$_3$ $>$ BH$_2$, provide a quantitative measure for the HCA of X relative to hydrogen.[8b] Three conclusions emerge: (a) the HCA increases as X is varied to the right along a row in the periodic table (OH deviates), but is only slightly changed as X is varied down a column (Cl deviates); (b) substituents with the same central atom, e.g., OH and OCH$_3$, or Me and Ph are expected to have similar HCA, provided that drastic changes in electronegativity (cf. CF$_3$, CN) are not made; (c) the HCA of X decreases if the population of the carbanionic orbital is reduced by charge delocalization to the α substituents. The rotational barrier in FCH$_2$C(CN)$_2^-$ is only 5.5 kcal/mol, roughly half of that in FCH$_2$CH$_2^-$. Intermediate conformations between **2a** and **2b** were also studied, confirming that the energy of **2** (relative to **2a**) at any angle θ is given by eq 2,[13] where θ is the XCCH$_a$ dihedral angle and V_x is the rotational barrier from Table I. Note that 0, 25, 75, and 100% of the full HCA of X are exerted at θ values of 0, 30, 60, and 90°, respectively. The decrease in $E(\theta)$ when θ changes from

Table I. Total Energies and Rotational Barriers for Several β-Substituted Ethyl Anions (STO-3G)

substituent (X = YH$_n$)	total energy of **2a**, hartrees[a]	V_X,[b] kcal/mol
BH$_2$	-102.31504^c	-4.9 (-6.2^h)
H	-77.39411^d	0
CH$_3$	-115.96992^c	2.1
NH$_2$	-131.70969^e	4.8
OH	-151.23683^c	11.5
OCH$_3$	-189.82313^f	12.6
F	-174.86321	10.1 (9.2^h)
SiH$_3$	-364.17243^c	-0.1
PH$_2$	-414.86889^e	4.1
SH	-470.58430^c	9.2
Cl	-531.44376	16.7
CN	-167.97838	6.3
CF$_3$	-408.38280	5.9
F, di-α-CN	-356.14030^g	5.5

[a] The details of the geometries and the effect of the variation of various geometric parameters on the energy will be given in the full paper. [b] $V_x = E(\mathbf{2b}) - E(\mathbf{2a})$. [c] $\angle$HYCC = 180°. [d] Fully optimized. [e] $\angle$HYCC = 60°. [f] $\angle$COCC = 180°. [g] For FCH$_2$C(CN)$_2^-$, with $r(C^-\!-\!CN) = 1.419$ Å and $r(C\equiv N) = 1.162$ Å taken from ref 10b. [h] From ref 12.

30 to 60° is thus twice as large as when it changes from 0 to 30° or from 60 to 90°. Equation 2 can be extended whereby the relative energy of any rotational conformer of the anion ZYXCCH$_2^-$ is calculated from eq 3.

$$E(\theta) = 0.5V_x(1 + \cos 2\theta) \qquad (2)$$

$$\begin{aligned} E(\theta) = \ & 0.5V_x(1 + \cos 2\theta) \\ & + 0.5V_y\,[1 + \cos 2(\theta + 120°)] \\ & + 0.5V_z\,[1 + \cos 2(\theta + 240°)] \end{aligned} \qquad (3)$$

Scheme I describes the mechanism of nucleophilic vinylic substitution[14] where the initially formed carbanion is **3** and products are formed by expulsion of LG from **5** or **9**.[1] Retained products (i.e., **10**) are observed if a 60° clockwise rotation around C_α-C_β (**3** $\rightarrow$ **4** $\rightarrow$ **5**) precedes the LG departure. A 120° counterclockwise rotation (**3** $\rightarrow$ **6** $\rightarrow$ **7** $\rightarrow$ **8** $\rightarrow$ **9**) which precedes a fast LG expulsion would lead to the inverted product **11**. Stereoconvergence results when internal rotation is fast and **5** and **9** equilibrate before LG expulsion.[15]

By applying the hyperconjugation model to Scheme I, assuming short-lived carbanions[15] and neglecting other effects on the stereochemistry, the following predictions are obtained. (i) A 30° clockwise rotation in **3** is preferred by $0.75(V_{LG} - V_R)$ kcal/mol over a 30° counterclockwise rotation (eq 3); retention via **3** $\rightarrow$ **4** $\rightarrow$ **5** $\rightarrow$ **10** is thus preferred when HCA(LG) $\gg$ HCA(R). (ii) Stereoconvergence prevails when

HCA(LG) ~ HCA(R). (iii) Inversion predominates when HCA(LG) ≪ HCA(R). (iv) The stereochemistry is independent of the nucleophile since the $C^-(2p)-(C-Nu)$ hyperconjugation is identically reduced by rotation in **3** in either direction. (v) Identical retention/inversion ratios should be obtained from E and Z precursors since HC imposes identical energetic requirements for the rotation of either of the isomeric carbanions **3** formed from these precursors. Different ratios are due to the involvement of other factors, e.g., eclipsing interactions in the elimination transition states. The following examples illustrate our conclusions. Consider the simple case—Nu = H^-, R = H, LG = Cl—where the calculated relative energies (STO-3G) of the carbanion's rotamers in kilocalories/mole are as follows: **3** (11.7), **4** (3.5), **5** (0), **6** (16.7), **7** (11.7), **8** (3.5), and **9** (0). The most stable conformations are **5** and **9** where $C^-(2p)-(C-Cl)$ HC is maximized, and the least stable is **6** where HC is zero. The 60° clockwise rotation **3 → 5** results in a continuous energy decrease, whereas in the counterclockwise rotation a barrier of 5 kcal/mol (**3 → 6**) has to be overcome before reaching conformer **9** and the inverted product **11**.[16] Likewise, retention is predicted for the reaction $HS^- + H_2C = CMeCl$,[17] where the relative energies of the $HSCMe(Cl)CH_2{}^-$-conformers are as follows: **3** (5.6), **4** (0.1), **5** (0), **6** (11.0), **7** (10.9), **8** (5.4), and **9** (0).[18] In view of conclusion iv, retention would also be predicted if the nucleophile was a labeled chloride ion. The exact shape of the potential surface for internal rotation in the carbanion is however nucleophile dependent. Thus in $Cl_2CMeCH_2{}^-$ the most stable conformer is **6** (**5**, for Nu = SH^-), and the energy difference between the most stable and least stable conformers is 14.5 kcal/mol (11.0 kcal/mol for Nu = SH^-). The predominance of retention decreases when HCA(LG) and HCA(R) become closer; e.g., when Nu = Me^-, R = SH, LG = F, retention is preferred over inversion by only 0.7 kcal/mol and additional factors (e.g., the C-LG bond strength) will affect the stereochemistry. When the HCA of all of the β substituents are similar (as in $MeOCF(OH)CHD^-$), the rotation barriers are effectively sixfold and small and stereoconvergence may be observed.[15]

The predominant retention observed in over 200 vinylic substitution reactions[1,2] is predicted by the hyperconjugation model since nearly always R = H, Ar, or alkyl and HCA(LG) ≫ HCA(R). The partial or complete stereoconvergence observed when Y = NO_2[19] also fits our model. The charge resides mainly on the α substituent and the rotational barrier is consequently low. We know of only three cases[20] where a good leaving group is displaced with partial stereoconvergence,[21] which we cannot explain by hyperconjugation. The situation is more complex for systems substituted by poor leaving groups, especially F, where the C-F bond cleavage is expected to be relatively slow and the carbanions are long lived.[1,2] Even if **5** is formed preferentially, rotation by 180° to **9** may still precede the LG explosion, giving stereoconvergence. This situation is more favorable with F where V is small compared to Cl or Br which have both high HCA and nucleofugacity. Depending on the lifetime of the carbanion, the α substituents, and the HCA of R and Nu, substitution of the poor leaving groups F,[5,22,23] NO_2,[24a] and SCN[24b] results in retention[22] or in partial[6b,23] or complete stereoconvergence.[5,24] When C_β carries two leaving groups, e.g., Cl and F, two different 60° rotations lead to conformers prone to elimination. The conformer with eclipsing Cl and $C^-(2p)$ is predicted to be formed preferentially, but the observed variety of products[22a,d,25] suggest the involvement of additional factors. Finally we note that inversion was never observed except for one special case,[26] in nucleophilic vinylic substitutions. In view of the HC theory this is not surprising. A "fast" leaving group such as Cl has a considerable higher HCA than the other substituents in Table I, so that the condition for inversion HCA(R) ≫ HCA(LG)

cannot be fulfilled. Even a poor LG such as F has a relatively high HCA. Furthermore, with poor leaving groups even in favorable cases for inversion, e.g., R = OCH_3, LG = F, other factors in addition to HC are dominant and stereoconvergence is predicted (see above).[27]

In conclusion, hyperconjugation is the major factor which determines the stereochemistry of nucleophilic vinylic substitution. The validity of this proposal should be further investigated in cases where incomplete retention is predicted or for substitution at C=N centers. Detailed analysis and more examples will be given in full paper.[28]

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(27) A referee has suggested that we will propose a suitable system which according to the HC theory will give inversion. With the substituents which were calculated in Table I, this cannot be achieved. Consideration of other groups which are not included in Table I, e.g., tosylate, involves severe assumptions which make a prediction of a case which should give inversion too speculative.

(28) NOTE ADDED IN PROOF. After the submission of our paper F. Texier, O. Henri-Rousseau and J. Bourgois published a related paper in *Bull. Soc. Chim. Fr., Ser. II*, 86 (1979). The approach of these authors is similar to ours but is totally *qualitative* and therefore does not allow analysis of borderline cases. Furthermore, neglect of the destabilizing $2p(C^-)-\sigma(X)$ interaction in **2a** may lead to erroneous conclusions, especially in comparing first- and second-row substituents.

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m-Quinomethane: Synthesis of a Covalent–Biradicaloid Pair of Valence Tautomers

Sir:

Two species comprise a covalent–biradicaloid pair when they respectively contain all and one less than all of the complement of bonds permitted by the standard rules of valence. Ring-cleavage reactions frequently implicate such pairs of valence tautomers (e.g., cyclopropane–trimethylene, methylenecyclopropane–trimethylenemethane), and, in general, the isomer of higher covalence is the more stable. However, in the case of the *m*-quinone[1] system symbolized by **1**, where the tautomers **2** and **3** differ by the presence or absence of the C-1–C-5 bond
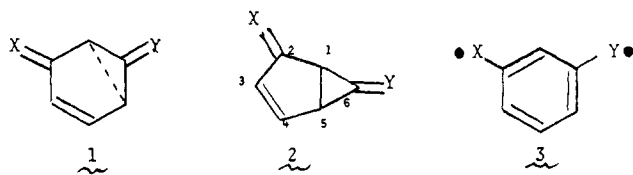

a:	X = Y = O
b:	X = O, Y = CH$_2$
c:	X = CH$_2$, Y = O
d:	X = Y = CH$_2$

(dashed line), the covalent form **2** will be destabilized by strain, whereas the biradicaloid form **3** will be stabilized by resonance. Thus, the two forms may not differ greatly in energy. Indeed rough bond additivity calculations[2] suggest that, in the case of *m*-quinomethane **1b**, the covalent tautomer **2b** actually is less stable than the biradicaloid one **3b** by ~4 kcal/mol. We report here directed preparations of the valency tautomers, **2b** and **3b**, of *m*-quinomethane, **1b**.[3]

Scheme I outlines a four-step synthesis of 6-methylenebicyclo[3.1.0]hex-3-ene-2-one (**2b**)[4-6] from cyclopentenone ethylene ketal. Pyrolysis of **2b** (15 m, 150 °C) in ethylene glycol gives the ether **4a**[7,8] in good yield. Similarly, **4a** and its analogue **4b**[4,7,8] are the major products of the photolyses of **2b**

Scheme I[a]
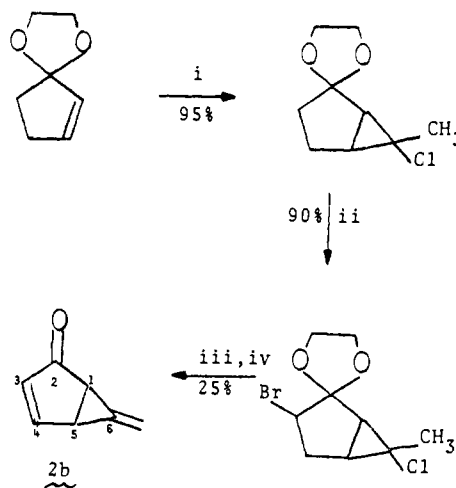
[a] (i) 2 equiv of BuLi, 2 equiv of CH$_3$CHCl$_2$, −30 °C, pentane, following a general procedure of S. Arora and P. Binger, *Synthesis*, 801 (1974); (ii) Br$_2$, Et$_2$O, 0 °C, following a general procedure of E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965); (iii) 4 equiv of KO-*t*-Bu, Me$_2$SO, 60 °C; (iv) Et$_2$O, 5% H$_2$SO$_4$.

(350 nm, 0 °C) in ethylene glycol or methanol solvents, respectively. Photolysis of **2b** in tetrahydrofuran or pyrolysis in *p*-cymene give only insoluble polymeric products. What role, if any, is played by **3b** in these reactions remains to be elucidated.

4a:	R = CH$_2$CH$_2$OH
b:	R = Me
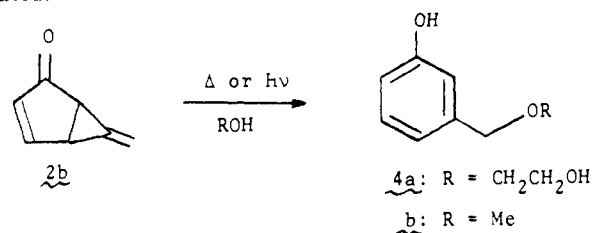
Irradiation at >310 nm of a degassed, glassy 0.29 M solution of dienone **2b** in 2-methyltetrahydrofuran at 11 K in the cavity of a Varian E-9 electron paramagnetic resonance (EPR) spectrometer (microwave frequency 9.064 GHz) for a few minutes gives rise to a well-defined triplet spectrum which persists for at least an hour. The spectrum, which consists of a group of six lines centered around 3260 G ($\Delta m_s = \pm 1$ transitions) and a weaker line near 1630 G ($\Delta m_s = \pm 2$), can be analyzed[10] in terms of the zero-field splitting (ZFS) parameters, $|D|/hc \simeq 0.027$ cm^{-1}, and $|E|/hc \simeq 0.008$ cm^{-1}, by using an anisotropic g tensor. When a 0.03 M solution of **2b** is irradiated at 77 K, no EPR signal is observed; however, inclusion of 0.25 M benzophenone leads to a triplet spectrum which, although weak, is identifiable as the same as that seen before, superimposed on a doublet impurity peak. A solution 0.3 M in **2b** and 0.25 M in benzophenone, acetophenone, or acetophenone-d_8 irradiated at 10 K gives a strong signal of the same triplet.

The most plausible candidate species for the carrier of the EPR spectrum is a triplet state of the *m*-quinomethane biradical, 3-methylenephenoxyl (**3b**). Two lines of argument, one exclusionary and one circumstantial, support the assignment.

A superficially attractive alternative might be an electronically excited triplet state of the bicyclic enone **2b**, but this is inconsistent with the long lifetime of the signal. Moreover, an enone triplet would be expected[11,12] to show a much larger $|D|/hc$ value (0.2–0.3 cm^{-1}) than that observed. Although theory[13-15] has been but little tested in this area and hence cannot be conclusive, approximate semiempirical