of the less efficient radical trap, a degenerate background reaction in which an acyl radical abstracts an aryltelluro group from an additional molecule of acyl telluride.[15] An alternative mechanism, suggested by a referee, in which PhSe$^{\bullet}$ PhS$^{\bullet}$, or **9** attacks at the carbonyl carbon of the acyl telluride with formation of a radical tetrahedral intermediate as in ArC(TeAr′)(SPh)O$^{\bullet}$ followed by expulsion of the aryltelluryl radical is unlikely given the high energy of the proposed intermediate radical with respect to the acyl telluride and attacking radical and given the cyclization results presented below (Chart I).

Irradiation of **3–5** in benzene at reflux gave the products of acyl radical cyclization with aryltellurium group transfer, **11–13**, in 96, 80, and 86% yields, respectively. The mass balance, in each case, was made up of the elimination product **15**. Photolysis of the acyl telluride **6** resulted in the formation of the cyclization product **14** in 90% yield after only 1.5 h. We view these cyclizations as radical chain reactions, with the two propagation steps being (i) cyclization of the unsaturated acyl radical and (ii) chain transfer by abstraction of an aryltelluryl group from an additional molecule of acyl telluride. The alternative possibility of attack of an aryltelluryl radical on the terminus of the allyl group followed by cyclization of the adduct radical onto the carbonyl group and expulsion of a chain carrying aryltelluryl radical, as has been demonstrated[16] for the superficially similar unsaturated acyltriphenylgermanes,[17] is unlikely. In particular the comparable ease of cyclization of **3** and **6** militates against this mechanism. When **4** was irradiated in the presence of diphenyl diselenide, and **9**, the trapping products **17** and **18** were isolated in 78 and 87% yields, respectively, indicating that trapping by these species competes effectively with cyclization. However, irradiation of **4** in the presence of diphenyl disulfide gave **12** in 90% yield, reinforcing the notion of the disulfide as a much poorer radical trap. Moreover, in none of these last three reactions was there any indication of products formed by attack of PhSe$^{\bullet}$, **9**, or PhS$^{\bullet}$ on the alkene terminus followed by cyclization of the adduct radical onto the acyl telluride moiety, reinforcing the notion that the observed chemistry is that of acyl radicals. The tellurium transfer products **11–13** were somewhat unstable, undergoing slow elimination to **15** on prolonged photolysis, on standing in air, and on silica gel chromatography. They could also be converted to **15** in excellent yield by simple stirring at room temperature with hydrogen peroxide in THF. Similarly, **14** was unstable decomposing slowly to **16**. Photolysis of the thiosalicylate derivative **19**, followed by chromatography on silica gel, gave the elimination product **20** in 41% yield.

Intermolecular carbon–carbon bond formation was achieved by photolysis of **2** in the presence of the allylic sulfide[18] **21**. The adduct **22**[19] was isolated from this reaction in 52% yield after 26 h at 8 °C. To date, although we have been able to prepare and isolate a number of stable acyl tellurides from aliphatic acids, we have been unable to induce them to undergo any radical chemistry, either thermally, photochemically (W and Hg), or with AIBN initiation. Our chemistry is therefore highly complementary to the acylcobalt chemistry of Pattenden[6] where problems were experienced with aromatic acids. We also anticipate that this facile method for the generation of aryl acyl radicals will be of use to those involved in fundamental spectroscopic studies of such species.[20]

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[19] With the exception of the tellurides **11–13** and **14**, which were characterized spectroscopically, all new compounds gave satisfactory spectroscopic and microanalytical or high-resolution mass data.

[20] Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869.

Radical Cation Photoisomerization of Bicyclo[2.2.2]octa-2,5-diene to Tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane and Its Thermal Retrogression

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Whereas the efficient photoisomerization of norbornadiene to quadricyclane has attracted interest and possible application as a means of storing solar energy,[1] it is the remarkably facile reverse reaction that has hitherto commanded attention in the radical cation chemistry of these valence isomers.[2-9] Thus, the norbornadiene radical cation product was readily detected following the ionization of quadricyclane in the gas phase,[2] in solution,[7] and in several solid matrices,[3,6,8] while the parent radical cation was not observed. Nevertheless, a discrete quadricyclane radical cation precursor, albeit short-lived, was implicated by pulse radiolysis[7] and CIDNP[4] studies on the one-electron oxidation of quadricyclane. Moreover, the formation of an excited state of the quadricyclane radical cation was recently proposed[9] as the primary photochemical step in the conversion of the norbornadiene radical cation to other bicyclic and monocyclic $C_7H_8{}^{\bullet+}$ isomers.[6,9] This interest in the intermediacy of the highly-strained quadricyclane radical cation prompted us to study the radical cations derived from the congeneric valence-isomer pair of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane[10] (**1**) and bicyclo[2.2.2]octa-2,5-diene[11] (**2**), and here we report the first direct spectroscopic evidence for the interconversion of **1**$^{\bullet+}$ and **2**$^{\bullet+}$.

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[11] (a) Although **1**$^{\bullet+}$ has not previously been identified, its formation was proposed as the first step in one of two alternate mechanisms used to describe the overall photorearrangement of **2**$^{\bullet+}$ to the 1,3,5,7-octatetraene radical cation, a transformation observed by electronic absorption spectroscopy in an argon matrix: Dunkin, I. R.; Andrews, L.; Lurito, J. T.; Kelsall, B. J. *J. Phys. Chem.* **1985**, *89*, 1701. (b) Reaction pathways for the stepwise photoisomerizations of **2**$^{\bullet+}$ and of the bicyclo[4.2.0]octa-2,4-diene radical cation in a Freon glass have also been formulated as proceeding initially through a benzene–ethylene radical cation π-complex assigned by electronic absorption spectroscopy: Fujisaka, Y.; Makino, M.; Takahashi, J.; Shida, T.; Roth, K.; Straub, R.; Bally, T. *J. Phys. Chem.* **1992**, *96*, 2205. Bally, T.; Roth, K.; Straub, R. *J. Am. Chem. Soc.* **1988**, *110*, 1639.

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Table I. Calculated ΔH_f Values, Bond Lengths, and ESR Parameters of $1^{\cdot+}$ and $2^{\cdot+}$

radical cation	ΔH_f,[a] kcal mol^{-1}	C1–C6,[a] pm	C1–C8,[a] pm	matrix	T, K	g_{iso}	nuclei	hyperfine couplings, G			ref
								exptl	AM1[a,b]	INDO[c]	
$1^{\cdot+}$	280.51	147.3	174.3	$CFCl_3$	129	2.0024 (6)	4 H_α[d]	5.7	3.3	6.6	this work
							2 H_β[e]	2.7	2.8	0.9	this work
$2^{\cdot+}$	236.95	138.3	229.6	$CFCl_3$	129	2.0029 (4)	4 H_{ol}[f]	6.85	4.97	4.23	this work
		(C2–C3)[g]	(C2–C6)[g]	$CFCl_3$	155	2.0030 (3)	4 H_{ol}[f]	6.76			12

[a] AM1–UHF calculations for energy-optimized geometries: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. [b] Calculated 1s spin densities after annihilation were multiplied by 1177 G: Clark, T.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 868. [c] Using the AM1–UHF optimized geometry as input and the INDO proportionality constant of 540 G to multiply 1s spin density: Pople, J. A.; Beveridge, D. L.; Dobosch, P. A. *J. Chem. Phys.* **1967**, *47*, 2026. [d] Hydrogens at the spin-bearing carbons C1, C6, C7, C8. [e] Hydrogens at C2, C5. [f] Hydrogens at olefinic carbons. [g] Based on numbering system for $2^{\cdot+}$.

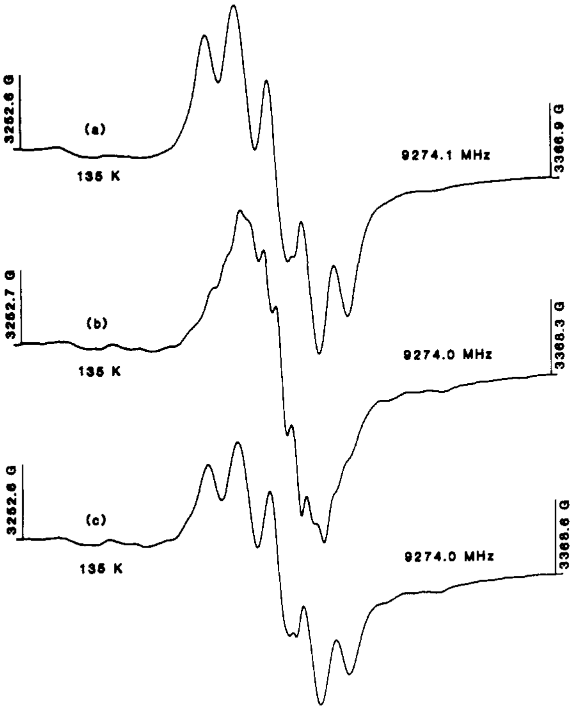


Figure 1. ESR spectra of a γ-irradiated (dose, 0.2 Mrad) solid solution of bicyclo[2.2.2]octa-2,5-diene in $CFCl_3$ recorded at 135 K under the same instrumental conditions before (a) and after exposure to visible light from a 1-kW tungsten lamp for 40 s (b) and after a further interval of 1 h at 135 K in the dark (c). The reduction in the signal intensity of $2^{\cdot+}$ from (a) to (c) can be attributed to the irreversible formation of a second photoproduct (spectral width ca. 108 G) in the first step of the cycle.

As previously reported,[12] the ESR spectrum of $2^{\cdot+}$ generated by radiolytic oxidation[13] in $CFCl_3$ (Figure 1a) and other Freon matrices consists of a quintet hyperfine pattern from coupling to the four equivalent olefinic hydrogens (a(4H) = 6.8 G). On exposure of the greenish-blue sample of $2^{\cdot+}$ in $CFCl_3$ to visible light, this quintet pattern was rapidly replaced by a quite different multiplet with much narrower line spacings (Figure 1b), clearly indicating the efficient formation of a photoproduct. Most interestingly, the subsequent thermal decay of the signal from this photoproduct at 135 K was accompanied by the restoration of the spectrum due to $2^{\cdot+}$ with ca. 70% of the original signal intensity (Figure 1c). Evidently, the photoproduct undergoes thermal retrogression to $2^{\cdot+}$ under these conditions.

The ESR spectrum of the photoproduct was recorded with higher resolution during continuous sample illumination (Figure 2a), and a good fit was obtained to the spectrum simulated in Figure 2b with input hyperfine parameters of 5.7 G (4 H) and 2.7 G (2 H). These values are in reasonable accord with the calculated parameters for $1^{\cdot+}$ (Table I). This spectral assignment of the photoproduct to $1^{\cdot+}$ is reinforced by the familial relationship between the photoproduct and $2^{\cdot+}$ implied by the thermal retrogression, as well as by the corresponding behavior of the quadricyclane–norbornadiene radical cation pair.[2–9] Accordingly, the interconversion reactions are depicted in Scheme I.

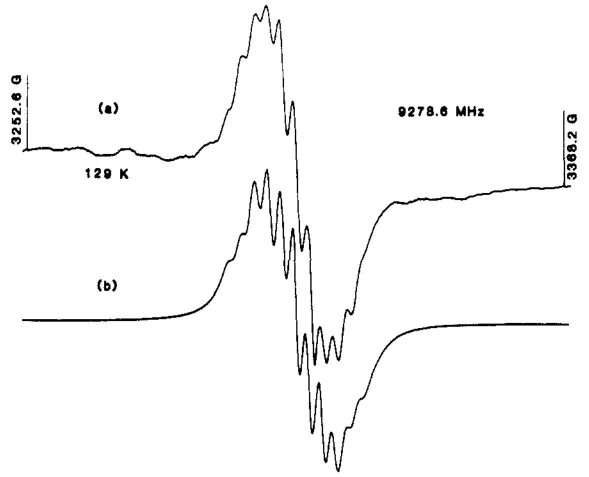
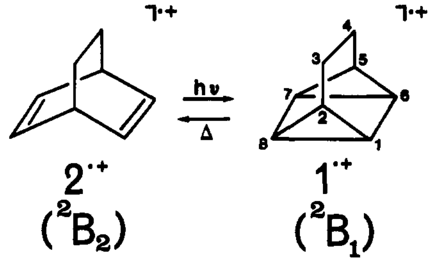


Figure 2. Comparison of the experimental ESR spectrum (see text and Figure 1b) assigned to $1^{\cdot+}$ (a) with its computer-simulated spectrum (b) according to the experimental hyperfine parameters given in Table I.

Scheme I



The thermal recovery of $2^{\cdot+}$ from $1^{\cdot+}$ ($t_{1/2}$ ca. 10 min at 135 K) is much slower than the corresponding growth of the norbornadiene radical cation following the pulse radiolysis of a quadricyclane solution at 96 K ($t_{1/2}$ of ca. 0.5 s).[7] A thermal activation barrier of 4.8 kcal/mol was estimated in the latter case, so that this comparison suggests that the barrier for the isomerization of $1^{\cdot+}$ to $2^{\cdot+}$ is substantially higher ($\Delta G^\ddagger \approx 9.5$ kcal/mol). Interestingly, this order of stability for the radical cations appears to be reversed for *neutral* derivatives of **1** and quadricyclane.[14–17] For example, the 1,6-bis(methoxycarbonyl) derivative of **1** (dimethyl tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane-1,6-dicarboxylate) produced by the photoisomerization of dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate undergoes thermal retrogression to the

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(14) For examples of thermally labile derivatives of **1** formed by photoisomerization of the corresponding bicyclo[2.2.2]octa-2,5-dienes, see: (a) Prinzbach, H.; Eberbach, W.; Philippossian, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 888. (b) Liu, R. S. H. *Tetrahedron Lett.* **1969**, 1409.

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(16) Prinzbach, H. *Pure Appl. Chem.* **1968**, *16*, 17; see especially pp 18 and 22 of this review.

(17) We thank a reviewer for directing attention to the switch in the relative thermal stability of the neutral molecules and radical cations of these two tetracyclic systems.

latter at 292 K ($t_{1/2}$ ca. 12 min, $\Delta G^{\ddagger} \approx 21.1$ kcal/mol),[14a] whereas quadricyclane derivatives, like quadricyclane itself ($t_{1/2} > 14$ h at 413 K, $\Delta G^{\ddagger} > 33.6$ kcal/mol),[16] are not thermally labile at room temperature. Since the activation barriers for the neutral molecules are much higher than those for the radical cations, the neutral transition states may reside further along the reaction coordinate. In this case, relief of strain could assume a dominant role in the neutral molecule reactions,[18] whereas altogether different structural factors might be expected to come into play for early transition states in the radical cation reactions.[19]

In summary, the present work has shown for the first time that the radical cation of a fused dicyclopropane ($1^{\bullet+}$) can be formed photochemically by cycloaddition from its diene radical cation counterpart ($2^{\bullet+}$). The observation of $1^{\bullet+}$ is also significant as a novel example of a radical cation identified with a highly strained and *previously unrealized* molecule.[10]

Acknowledgment. We thank Professor Thomas Bally for his comments on the preprinted version of this paper. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy (Grant No. DE-FG05-88ER13852).

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(18) Computational results[10] suggest that the heat of reaction for the cleavage of neutral 1 is more exothermic than that of quadricyclane by ca. 10 kcal/mol. Accordingly, the greater reactivity shown by the neutral derivatives of 1 relative to those of its lower homologue is in keeping with a late transition state accompanied by relief of strain. Cf. Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.

(19) An early transition state for the cleavage of the radical cations may be associated with a surface crossing from a $^2B_1$ to a $^2B_2$ state.[3]

A Dibenzofuran-Based Amino Acid Designed To Nucleate Antiparallel β-Sheet Structure: Evidence for Intramolecular Hydrogen-Bond Formation

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Received May 20, 1992

β-Sheets are found in almost all proteins, yet this secondary structure is poorly understood when compared to the α-helix.[1] We have recently reported the synthesis of amino acid 1 as part of our effort to develop small antiparallel β-sheets which are amenable to biophysical examination.[2a] The dibenzofuran-based amino acid was designed to form a specific intramolecular hydrogen bond of the type that will nucleate β-sheet formation within a polypeptide sequence.[3] We now report ^{1}H NMR and FT-IR evidence for an intramolecular hydrogen bond of this nature in diamide derivatives of 1.[2b]

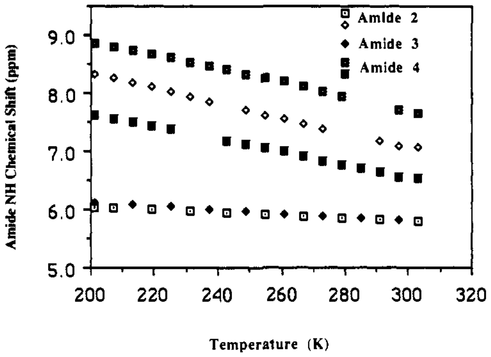
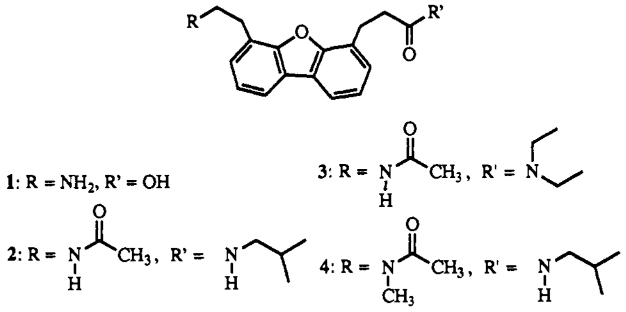


Figure 1. Temperature dependence of the amide proton NMR chemical shift for diamides 2, 3, and 4 in 1.5 mM CD_2Cl_2 solutions. Alternate data points for diamides 2 and 3 (around δ 6 ppm) were omitted for clarity. Data points around δ 7.2 ppm and δ 7.8 ppm are missing due to overlap with the aromatic region of dibenzofuran. The data were obtained on a Varian XL-400 spectrometer.



The ability of amides composed of 1 to undergo intramolecular hydrogen bonding in nonpolar solvents at room temperature is required, but is not sufficient, to predict their efficacy as nucleators in aqueous solutions. Other factors such as optimized geometry and hydrophobic interactions also play an important role in aqueous solvents. This paper presents evidence that satisfies the hydrogen-bonding criteria that a sheet nucleator must meet.[3,4] In order to examine the potential of amino acid 1 to nucleate antiparallel β-sheet formation, diamide 2 was synthesized. The degree of intramolecular amide–amide hydrogen bonding was determined by analyzing the temperature dependence of the amide proton NMR chemical shift and the amide N–H IR stretch region (3200–3500 cm^{-1}).[5]

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(1) See: Creighton, T. E. *Proteins—Structures and Molecular Principles*; W. H. Freeman and Co.: New York, 1984; p 191.

(2) (a) Díaz, H.; Kelly, J. W. *Tetrahedron Lett.* **1991**, *32*, 5725. (b) Diamides 2 and 3 were prepared from the *t*-Boc pentafluorophenol active ester of 1 and the corresponding amine followed by TFA deprotection and acetylation. Diamide 4 was prepared by methylation of the *t*-Boc derivative of 1 as described in ref 2c. All compounds were purified by crystallization or RP-HPLC and characterized by NMR and high-resolution mass spectroscopy. Full experimental details will be published elsewhere. (c) Cheung, S. T.; Benoiton, N. L. *Can. J. Chem.* **1977**, *55*, 906.

(3) According to studies reported recently, the incorporation of a rigid template (with the appropriate dimensions and geometry) into a polypeptide strand should decrease the chain entropy penalty associated with the nucleation of secondary structures. For details, see: (a) Kemp, D. S.; Curran, T. P.; Davis, W. M.; Boyd, J. G.; Mundel, C. *J. Org. Chem.* **1991**, *56*, 6672. (b) Kemp, D. S.; Curran, T. P.; Boyd, J. G.; Allen, T. J. *J. Org. Chem.* **1991**, *56*, 6683. (c) Kemp, D. S.; Boyd, J. G.; Mundel, C. *Nature* **1991**, *352*, 451. (d) Williams, D. H.; Cox, J. P. L.; Doig, A. J.; Gardner, M.; Gerhard, U.; Kaye, P. T.; Lal, A. R.; Nicholls, I. A.; Salter, C. J.; Mitchell, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 7020.

(4) For references related to the design, synthesis, and evaluation of β-turn mimetics, see: (a) Hölzemann, G. *Kontakte* **1991**, 3. (b) Hölzemann, G. *Kontakte* **1991**, 55. (c) Ernest, I.; Kalvoda, J.; Rihs, G.; Mutter, M. *Tetrahedron Lett.* **1991**, *31*, 4011. (d) Kemp, D. S. *Trends Biotechnol.* **1990**, *8*, 249. (e) Kemp, D. S.; Bowen, B. R.; Muendel, C. C. *J. Org. Chem.* **1990**, *55*, 4650. (f) Olson, G. L.; Voss, M. E.; Hill, D. E.; Kahn, M.; Madison, V. S.; Cook, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 323. (g) Brandmeier, V.; Feigel, M. *Tetrahedron* **1989**, *45*, 1365. (h) Feigel, M. *Liebigs Ann. Chem.* **1989**, 459. (i) Kahn, M.; Bertenshaw, C. M. *Tetrahedron Lett.* **1989**, *30*, 2317. (j) Kahn, M.; Wilke, S.; Chen, B.; Fujita, K. *J. Am. Chem. Soc.* **1988**, *110*, 1638. (k) Kemp, D. S.; Bowen, B. R. *Tetrahedron Lett.* **1988**, *29*, 5077. (l) Kemp, D. S.; Stites, W. E. *Tetrahedron Lett.* **1988**, *29*, 5057. (m) Kahn, M.; Chen, C. M. *Tetrahedron Lett.* **1987**, *28*, 1623. (n) Feigel, M. *J. Am. Chem. Soc.* **1986**, *108*, 181. (o) Kahn, M.; Devens, B. *Tetrahedron Lett.* **1986**, *27*, 4841. (p) Sato, K.; Nagai, U. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1231. (q) Kemp, D. S.; McNamara, P. E. *J. Org. Chem.* **1985**, *50*, 5834. (r) Nagai, U.; Sato, K. *Tetrahedron Lett.* **1985**, *26*, 647. (s) Kemp, D. S.; McNamara, P. E. *J. Org. Chem.* **1984**, *49*, 2286. (t) Kemp, D. S.; Sun, E. T. *Tetrahedron Lett.* **1982**, *23*, 3759. (u) Krstenansky, J. L.; Baranowski, R. L.; Currie, R. L. *Biochem. Biophys. Res. Commun.* **1982**, *109*, 1368. (v) Freidinger, R. M.; Verber, D. F.; Schwenk-Perlow, D. *Science* **1980**, *210*, 656. (w) Nowiak, J. S.; Powell, N. A.; Martinez, E. J.; Smith, E. M.; Noronha, G. *J. Org. Chem.* **1992**, *57*, 3763.

(5) (a) Gellman, S. H.; Adams, B. R.; Dado, G. P. *J. Am. Chem. Soc.* **1990**, *112*, 460. (b) Gellman, S. H.; Dado, G. P.; Liang, G.; Adams, B. R. *J. Am. Chem. Soc.* **1991**, *113*, 1164. (c) Liang, G.; Dado, G. P.; Gellman, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 3994.

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