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Photochemistry of Benzylidene-*d*,*l*-piperitones in Solution and the Melt Phase

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The solution- and melt-phase photochemistry of four *trans*-benzylidene-*d*,*l*-piperitones (**1**) has been investigated under a variety of conditions. The **1** undergo trans ⇌ cis isomerization to establish a quasi photostationary state. Further irradiation leads to **2** via oxidative ring closure. Conspicuously absent are dimers (obtained upon irradiation of the neat crystals) and the plausible Norrish Type II photoproducts, **3**. Although **1c** yields **2c**, no evidence for the alternative cyclization route to **2a** (requiring loss of HCl) has been observed. Rationalizations for the transformations are presented. The structure of **2b** has been determined unambiguously from X-ray crystallographic analysis.

Introduction

Our interest in the steering ability of halogens, especially chlorine and bromine, in solid-state reactions led us to examine the photoreactions of four *trans*-benzylidene-*d*,*l*-piperitones (**1**).[1] The exclusive solid-state products isolated from irradiation of **1** were dimers. Since conformational freedom is increased enormously in the liquid phases, we decided to determine the fate of electronically excited **1** in dilute solutions and in the melt.

A priori, several unimolecular photochemical pathways might be available to **1** in the liquid state in addition to photodimerization. These include trans ⇌ cis isomerization, oxidative cyclization[2] of *cis*-**1** to yield **2**, and Norrish Type II elimination[3-5] to form **3** (Scheme I). Of these, only geometric isomerization and cyclization have been detected here. Both are interesting mechanistically,[2c,6,7] and the photocyclization is an important tool in the syntheses of natural products[8] such as phenanthrene derivatives[9] and alkaloids.[10] Although **1c** can be envisioned to cyclize in two ways—at the protonated ortho carbon of the benzylidene ring to yield **2c** or the chlorinated ortho carbon to yield **2a**[11]—the former pathway dominates. Proof of the structures of **2** comes from analyses of their ^{1}H NMR, IR, UV, and mass spectra (Table I). In addition, the X-ray crystallographic structure of **2b** has been determined and is reported here.

Results and Discussion

Based upon several experimental observations and by analogy with the photochemistry of related compounds, the probable mechanistic pathway from *trans*-**1** to **2** is described by Scheme II.[2,12] For example, irradiation of **1b** in oxygen-saturated methanol led to a decrease in its concentration and an increase of a compound present initially in very small amounts (analyses by HPLC). A quasi-photostationary state between *trans*-**1b** and the new compound was established relatively rapidly. We assume, reasonably,[13,14] that the new compound is *cis*-**1b**. The time profile for its growth and decay is included in Figure 1. The reactions are remarkably clean; even at very high percent conversions of *trans*-**1**, only traces of compounds other than *cis*-**1** and **2** were detected by HPLC analyses.

The temporal composition changes in Figure 1 have been calculated from HPLC peak areas and knowledge of the molar extinction coefficients of *trans*- and *cis*-**1b** at the detector wavelength (300 nm). Thus, after 2.7 mg of **1b** in 0.5 mL $CDCl_3$ had been irradiated for a short period, a ^{1}H NMR spectrum was recorded. The ratio of *trans*/*cis* was calculated to be 2/3 based upon integration of the singlets from the enone proton in each isomer (~6 ppm). The contents of the tube were diluted so that the total concentration of **1b** was 2×10^{-5} M. Its UV spectrum (curve 2 of Figure 2) may be compared to that of unirradiated *trans*-**1b** (8×10^{-6} M; curve 1). Subtraction of curve 1 from curve 2 yields curve 3, the absorption spectrum of 1.2×10^{-5} M *cis*-**1b**: λ_{max} 290 nm and ϵ_{max} 27 500 are calculated for *cis*-**1b**. This hypsochromic shift and decreased molar extinction coefficient for the cis isomer relative to the trans (see Table I) follows the relationship reported between cis and trans isomers of related molecules.[14a,15] As expected, the photochemistry of the cis isomers of these molecules depends upon several factors, including the wavelength of excitation and the energy minima of rotamers.[14-18]

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Scheme I

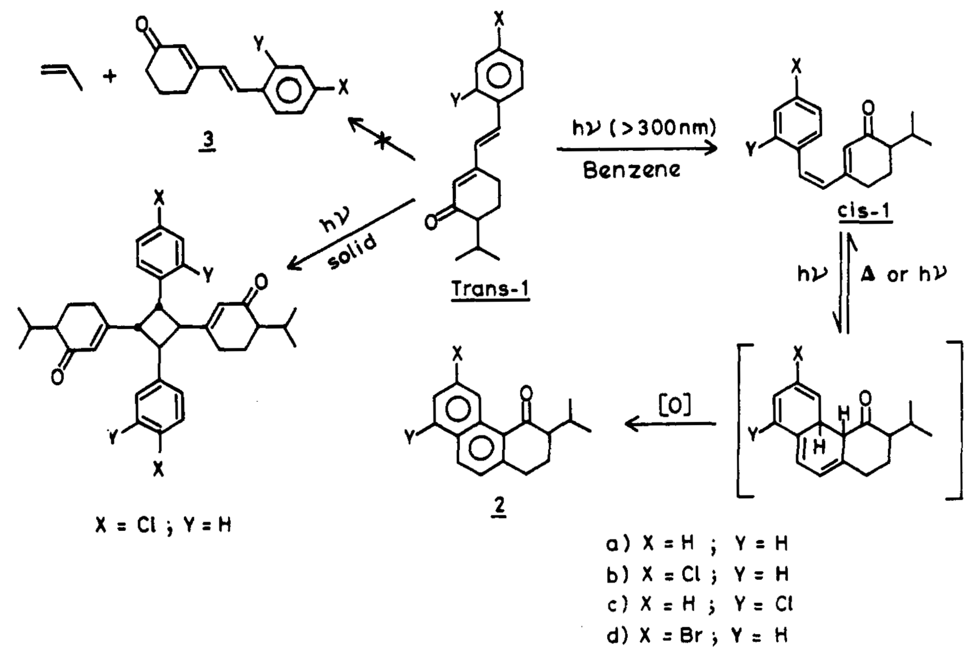

Table I. Spectroscopic Data for 1 and Associated Molecules

compd	mp (°C)	^{1}H NMR, δ (*J* in Hz)	IR (Nujol), cm^{-1}	UV, nm (ε), in MeOH	mass spectra (*m*/*e*)
1a	58	0.86 (d, *J* = 6.5, 3 H), 0.98 (d, *J* = 6.5, 3 H), 1.45–3.00 (m, 6 H), 6.04 (s, 1 H), 6.72 (d, *J* = 17.6, 1 H), 7.08 (d, *J* = 17.6, 1 H), 7.20–7.60 (m, 5 H)	1659, 1623, 1590	321 (35 500), 235 (9400)	
1b	97	0.84 (d, *J* = 7.2, 3 H), 0.96 (d, *J* = 7.2, 3 H), 1.80–2.96 (m, 6 H), 6.02 (s, 1 H), 6.74 (d, *J* = 18, 1 H), 6.94 (d, *J* = 18, 1 H), 7.20–7.80 (m, 4 H)	1664, 1615, 1595	324 (41 700), 236 (9700)	
1c	64	0.88 (d, *J* = 6.1, 3 H), 0.98 (d, *J* = 6.1, 3 H), 1.48–3.0 (m, 6 H), 6.04 (s, 1 H), 6.76 (d, *J* = 16.2, 1 H), 7.02 (d, *J* = 16.2, 1 H), 7.20–7.80 (m, 4 H)	1660, 1610, 1590	316 (28 500), 237 (9500)	
1d	112	0.82 (d, *J* = 7.9, 3 H), 0.98 (d, *J* = 7.9, 3 H), 1.72–2.84 (m, 6 H), 6.04 (s, 1 H), 6.76 (d, *J* = 18, 1 H), 7.04 (d, *J* = 18, 1 H), 7.20–7.58 (m, 4 H)	1662, 1623, 1581	326 (38 800), 237 (8500)	
2a		0.92 (d, *J* = 6.8, 3 H), 1.0 (d, *J* = 6.8, 3 H), 1.80–2.64 (m, 4 H), 3.0–3.24 (m, 2 H), 7.20–8.08 (m, 5 H), 9.20 (d, *J* = 7.3, 1 H)	1668, 1623, 1602	306 (8800), 231 (47 200)	238, 196
2b	71	0.90 (d, *J* = 6.8, 3 H), 0.98 (d, *J* = 6.8, 3 H), 1.76–2.56 (m, 4 H), 2.94–3.20 (m, 2 H), 7.08–7.88 (m, 4 H), 9.28 (s, 1 H)	1664, 1615, 1595	310 (8900), 226 (50 800)	274, 272, 230
2c		0.84 (d, *J* = 5.8, 3 H), 0.94 (d, *J* = 5.8, 3 H), 1.72–2.60 (m, 4 H), 2.88–3.20 (m, 2 H), 7.12–8.00 (m, 3 H), 8.32 (d, *J* = 9.0, 1 H), 9.02 (dd, *J* = 3.2, 7.2, 1 H)	1680, 1614, 1596	313 (8500), 221 (35 200)	274, 272, 230
2d	79	0.96 (d, *J* = 5.4, 3 H), 1.02 (d, *J* = 5.4, 3 H), 1.54–2.60 (m, 4 H), 2.96–3.08 (m, 2 H), 7.20–8.00 (m, 4 H), 9.48 (s, 1 H)	1674, 1614, 1590	312 (8800), 231 (47 200)	318, 316, 274
3b	93	1.82–2.26 (m, 2 H), 2.28–2.72 (m, 4 H), 6.08 (s, 1 H), 6.76 (d, *J* = 18, 1 H), 7.0 (d, *J* = 18, 1 H), 7.24–7.52 (m, 4 H)	1653, 1617, 1581	324 (41 700), 237 (9400)	

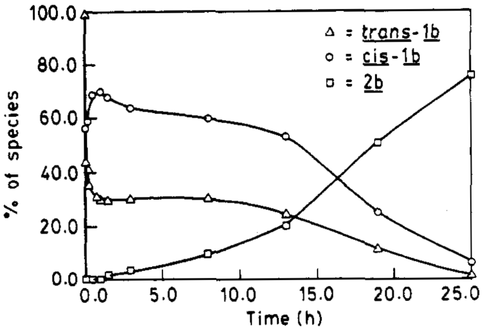

Figure 1. Percent composition of an irradiated solution of **1b** versus time.

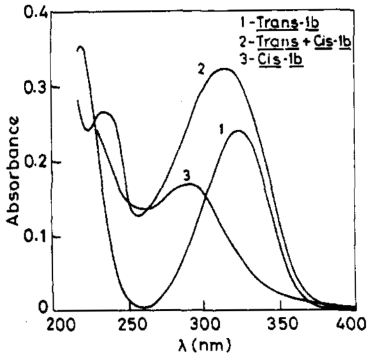

Figure 2. Absorption spectra of the trans and cis isomers of **1b**. The cell width is 1 cm.

An expected reaction of *cis*-**1** is a photoinitiated electrocyclic transformation leading to dihydro **2**. As in the stilbene–phenanthrene photoconversion,[2c,12,18] the dihydro intermediate should be very unstable. Although analogous intermediates have been detected in solution via their visible absorption spectra (400–500 nm),[2c,19] they have not

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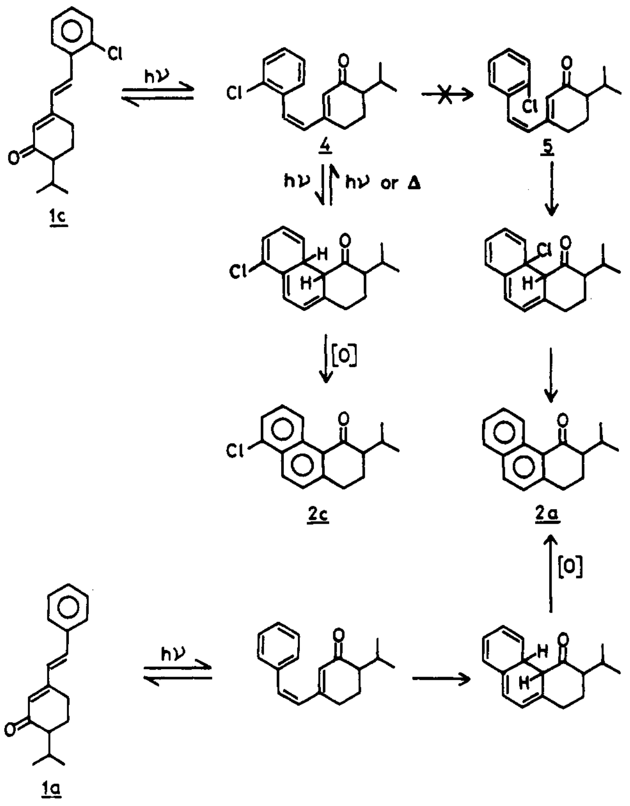
Scheme II



been isolated: dihydrophenanthrene is extremely sensitive to molecular oxygen; it can revert thermally or photochemically to *cis*-stilbene.[20] Substitution of the bridghead hydrogen atoms for alkyl groups[21] or rapid conversion of the dihydrophenanthrene to a more stable species[22] has led to isolatable intermediates. None of these mitigating factors should be operative in intermediates derived from 1.

Consistent with our expectations, several of our attempts to detect dihydro 2 were unsuccessful. Thus, a sample of **1b** in nitrogen-saturated $CDCl_3$ was tightly capped, immersed in an ethanol-liquid N_2 mixture, and irradiated with the output from a Hanovia 450-W medium-pressure mercury vapor lamp for 30 min. Periodically, the tube was transferred rapidly to the probe of our NMR spectrometer and spectra were recorded at room temperature. The resonances could be assigned exclusively to *trans*- and *cis*-**1b** and to **2b**. The structure of **2b** is known unambiguously from X-ray crystallographic determinations (see Experimental Section).

Another possible photoproduct from **1** is **3** if Norrish type II elimination occurs. However, such processes are efficient only in ketones which possess lowest n,π^* singlet or triplet excited states.[3-5] The high molar extinction coefficients of the lowest energy absorption bands of **1** indicate that the first excited singlet states are π,π^*; other ketones with extended conjugation have been shown to possess lowest energy triplet states with π,π^* configurations.[23] Thus, no **3** is expected from irradiations of **1**. To be certain, **3b** was synthesized independently and its HPLC retention volume was compared with those from peaks in a chromatogram of irradiated **1b**. None of the peaks from the irradiated **1b** sample were in the vicinity of the **3b** peak. In principle, the photocyclization product from **1c** can be either **2a** or **2c**. Cyclization of *cis*-**2c** involving the chlorinated carbon of the benzylidene ring and subsequent elimination of HCl would result in **2a**;[11] the formation of **2c** can be envisaged as a consequence of cyclization with participation of the other ortho carbon of the benzylidene ring and oxidative loss of two hydrogen atoms. Under a variety of reaction conditions, the sole cyclization product detected from **1c** was **2c**. These included irradiation of a nitrogen-saturated solution of **1c** in: (1) methanol (yielding traces of **2c** due to the presence of residual molecular oxygen); (2) methanol containing a small amount of Na_2CO_3; (3) 1/20 (v/v) pyridine/methanol; (4) pyridine; and (5) methanol containing 0.5 M sodium methoxide.

The absence of **2a** may be attributable to a much higher energy of rotamer **5** than **4** (leading to a very low probability of formation of the **2a** cyclized precsursor[18]), rapid reversion of the cyclized intermediate to **5**, or its inefficient loss of HCl. Molecular mechanics calculations (MMX force field incorporated into the PC MODEL program[24]) exploring the energy dependence of *cis*-**1c** on rotation about the ethenyl-chlorophenyl σ-bond reveal that **5**, the family of rotamers expected to lead to **2a**, are much more energetic than the family of **4** rotamers.[24b] Although the level of sophistication of these calculations is low and the exact coordinates of the minimized geometries are probably different from those encountered in solution, the preference for **4** over **5** is clear and compelling. Thus, although the other factors mentioned above may also disfavor formation of **2a** from *cis*-**1c**, they need not be invoked since cyclization is expected to yield the **2c** precursor almost exclusively.

Since irradiation of neat, solid *trans*-**1** yields photodimers rather than *cis*-**1** and **2**,[1] experiments were conducted to determine the selectivity of this topochemical process. Thus, crystals of **1b** and **1d** were heated to slightly above their melting points and irradiated. No dimer, cis isomer, or **2** was detected. Only *cis*-**1** and **2** (no photodimer) were detected from irradiations at room temperature of very concentrated solutions of **1b** and **1d** (i.e., 5 mg of **1** and 2 drops of $CDCl_3$), indicating that the relatively high temperatures of the neat irradiations were not responsible for the lack of photodimers; the unimolecular rearrangements are intrinsically faster than their bimolecular counterparts when the reaction media allow the necessary intramolecular motions to occur. Analogous competitions between unimolecular and bimolecular excited-state reactions have been reported for many molecules, including acyclic and cyclic enones, in the solid state.[25] Whereas the acyclic molecules usually undergo intramolecular cycloaddition reactions in solution with great difficulty, the cyclic enones yield cyclodducts from solution irradiations with reasonable chemical yields and high quantum efficiencies.[23]

Conclusions

We have demonstrated that liquid-phase photochemical reactions of a series of *trans*-benzylidene-*d*,*l*-piperitones differ completely from those observed in the crystalline

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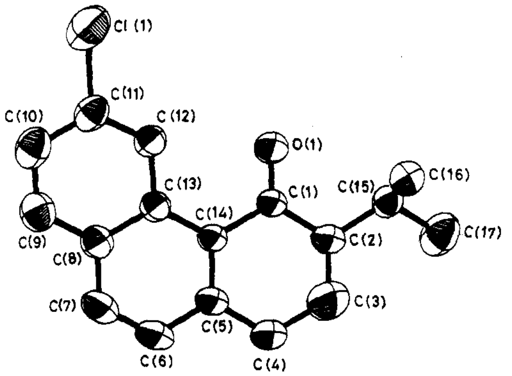

Figure 3. A perspective view of **2b** with atomic numbering scheme.

state.[1] The processes observed in solution mimic stilbene → phenanthrene transformations; dimerizations dominate in the solid. The ease and efficiency of the transformations of 1 to 2 demonstrate the synthetic utility of these photoreactions. The structure of the cyclization photoproduct **2b** (from **1b**) has been determined unambiguously, and the other 2 can be related to it by their spectroscopic characteristics.

Consistent with the expected π,π^* configurations of the lowest excited singlet and triplet states of 1, no Norrish Type II products (like **3**) could be detected. Also, no **2a** was observed upon irradiation of **1c** under a variety of conditions. According to molecular mechanics calculations, the absence of the dehydrochlorination product is a consequence of the high energetic prejudice against rotamer **5** of *cis*-**1c**. Even in the neat melt, no photodimers were detected from 1.

These results constitute a clear-cut example of the importance of conformations (molecular shapes) and intermolecular spatial relationships (translations, rotations, etc.) on the selectivity of photoinduced reactions of related multifunctional molecules.

Experimental Section

Instrumentation. Melting points were recorded on a Reichert-Kofler micro heating stage with a microscope and are uncorrected. Analytical HPLC was performed with a Schimadzu gradient-elution chromatograph using a (UV/vis detector; 300 nm), a Shimpack CLC ODS column (6 × 150 mm; 5-μm particles), and methanol–water as the eluant (linear gradient). ^1H NMR spectra ($CDCl_3$; TMS) were recorded on a JEOL FX-90Q FT spectrometer: chemical shifts are reported in ppm from TMS. IR spectra of Nujol mulls were recorded on a Hitachi 270-50 IR spectrophotometer. UV/vis absorption spectra were recorded on a Shimadzu UV-180 spectrophotometer using matched 1-cm quartz cuvettes. Mass spectra were taken on a JEOL MS-DX 303 mass spectrometer operating in the electron impact mode (70 eV). Unless indicated otherwise, irradiations were conducted with the Pyrex-filtered output of a Rayonet reactor ($\lambda > 300$ nm). A fan circulated cool air through the reactor, maintaining the ambient temperature below 28 °C.

Materials. The benzylidene-*d,l*-piperitones were prepared by a standard procedure.[26] Only **1a**, with mp 59–60 °C,[26] has been reported previously. The physical properties of the other 1, 2, and **3b** are included in Table I. Benzene (Ranbaxy Laboratories) was purified by shaking it sequentially with concd H_2SO_4 (4X), water, dilute aqueous $NaHCO_3$, and water. It was dried ($CaCl_2$), distilled, and finally distilled from sodium ribbon. Methanol (S.D. Fine Chemicals, analytical grade containing 0.1% water) was used as received.

Solution-Phase Irradiations. In a typical procedure, 20 mg of **1b** in 40 mL of benzene was irradiated in a stoppered Pyrex vessel. The progress of the reaction was monitored periodically by UV spectroscopy and thin-layer chromatography (TLC). After 36 h, the solution was concentrated to ~10% of its original volume on a steam bath. Careful separation of the photoproducts by preparative TLC (2/3 chloroform/hexane) yielded 14 mg (71%) of **2b**, a pale yellow solid, mp 71 °C. The isolated yields of the photoproducts from the other 1 were 61% (**2a**), 65% (**2c**), and 76% (**2d**).

Melt-Phase Irradiations. A film of **1b** (mp 97 °C) was made by placing 20 mg of it in a 25-mL beaker and placing the bottom of the beaker in a bath of hot (105–107 °C) liquid paraffin. Irradiations were conducted as before, and aliquots of the melt were analyzed periodically by dissolving them in $CDCl_3$ and recording their proton NMR spectra. Neither the dimer[1] nor cyclization product **2b** could be detected. Similar results were obtained with a **1b** melt irradiated under a nitrogen atmosphere, and with a **1d** melt, irradiated under air or nitrogen.

Attempts To Detect 3b. A sample of **1b**, but lacking the isopropyl group, was synthesized as before[26] in 55% yield and irradiated to produce **3b**, mp 93 °C (Table I). An HPLC analysis of 5 mg of **1b** in 10 mL of benzene which had been irradiated for 36 h indicated the presence *trans*- and *cis*-**1b** and **2b**; no peak near the retention volume of **3b** was observed.

X-ray Structure Determination of 2b. Good single crystals of **2b** were obtained from methanol by slow evaporation. Intensity data of **2b** were collected on an Enraf Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation to a θ limit of 25° in $/2\theta$ mode. Out of 2970 unique reflections, 2001 were considered significant with $|F_o| > 4\sigma|F_o|$. The data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved using the direct methods program SHELX-86[27] and refined with the full-matrix least-squares method using SHELX-76.[28] Refinement of the positional and anisotropic thermal parameters of non-hydrogen atoms, except for those of C(2) and C(3), and employing a unit weighting scheme converged to a final R value of 0.061. Since the hydrogens of C(2) and C(3) atoms could not be located from the difference Fourier, they were stereochemically fixed, but not refined due to the very high thermal motion associated with the carbon atoms. The final difference Fourier map was featureless with $\Delta\rho_{max} = 0.31$ and $\Delta\rho_{min} = -0.50$ e/Å^3. A perspective view of **2b** with the numbering scheme used is given in Figure 3.

Crystal data: $C_{17}H_{17}OCl$, $M_r = 272.8$, triclinic, $P\bar{1}$, $a = 8.079$ (1) Å, $b = 9.469$ (2) Å, $c = 10.150$ (1) Å, $\alpha = 100.49$ (1)°, $\beta = 78.01$ (1)°, $\Gamma = 74.83$ (2)°, $V = 709.7$ (5.0) Å^3, $Z = 2$, $D_m = 1.27$, $Dx = 1.276$ g/cm^3, Mo Kα, $\lambda = 0.7107$ Å, $\mu = 2.15$ cm^{-1}, $F(000) = 288$, $T = 293$ K, $R = 0.061$ for 2001 observed reflections.

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Registry No. *dl-trans*-**1a**, 109827-70-5; *dl-trans*-**1b**, 131956-49-5; *dl-cis*-**1b**, 137232-08-7; *dl-trans*-**1c**, 137174-72-2; *dl-trans*-**1d**, 136286-77-6; *dl*-**2a**, 137174-73-3; *dl*-**2b**, 137174-74-4; *dl*-**2c**, 137174-75-5; *dl*-**2d**, 137174-76-6; *dl*-**3b**, 54107-08-3.

Supplementary Material Available: Positional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms of **2b**, interatomic distances of **2b** as determined by X-ray crystallography, and positional coordinates of hydrogen atoms of **2b** (4 pages). Ordering information is given on any current masthead page.

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