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1-Benzylidene-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-trienes: Synthesis and Photochemistry of a Series of Optically Active Potential Triggers for Physical Amplification of a Photoresponse in Liquid Crystalline Media

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Introduction

Photochemical reactions provide special advantages in the control of processes that are difficult or impossible to achieve by use of conventional thermal reactions. In particular, light-initiated processes can play a special role in information transfer and in signal transduction. This is possible because light can carry information by modulation of intensity (on and off, for example), wavelength, or polarization. Moreover, light generated external to a reaction vessel may be steered to specific domains within the vessel's interior and used to trigger specific chemical or physical changes at specified locations. For example, in vision[1] a light-initiated cis to trans isomerization triggers a series of structural and chemical events resulting, eventually, in perception. The sensitivity achieved by the visual apparatus highlights an important requirement for the efficient utilization of photochemical reactions for information transfer or storage. Since light is "dilute", its effect must be amplified by subsequent chemical or physical processes.

We have undertaken a research project directed toward development of new materials that may prove to be suitable for photochemically-based information storage. In our approach, information would be coded in the polarization of light and the effect of the photochemical trigger would be amplified by the reversible conversion of a liquid crystalline material between nematic and cholesteric forms.[2] Specifically, irradiation of a selected racemic compound (the dopant) with circularly polarized light will induce an enantiomeric excess (ee) in the mixture.[3] Conversely, irradiation of the optically active mixture with unpolarized light will regenerate the racemic form. Since conversion of a racemate to an optically active mixture converts a nematic liquid crystal to the cholesteric form and vice versa,[4] the alternate exposure of the dopant dissolved in a liquid crystalline medium to circularly polarized and unpolarized light will trigger a physical change in the liquid crystal and provide a means for amplification and sensing of the photochemical reaction.

$$p = [\beta_M C\gamma]^{-1} \tag{1}$$

$$[\mathrm{ee}]_{\mathrm{PSS}} = g_\lambda/2 \tag{2}$$

This approach to light-based information storage hinges on the successful discovery of suitable dopants since their irradiation with circularly polarized light must generate an ee sufficiently large to trigger a detectable transition in the liquid crystal. Our previous experiments reveal that a pitch (p) of ca. 100 μm in a cholesteric liquid crystal is the practical limit for simple optical detection of this phase.[5] The pitch of a cholesteric liquid crystal formed by addition of an optically active dopant to a nematic phase is determined by the optical purity of the dopant (γ), its helical twisting power (β_M), and its concentration (C, mol of dopant/mol of solution) according to eq 1. The enantiomeric excess at the photostationary state $\{[\mathrm{ee}]_{\mathrm{PSS}}\}$ for optical isomerization between enantiomers irradiated with circularly polarized light is determined by $g_\lambda = (\Delta\epsilon/\epsilon)$ according to eq 2. Consequently, our search for a suitable dopant is directed to compounds that possess β_M and g_λ values sufficiently large to generate a pitch of at least 100 μm in a cholesteric liquid crystal.

In addition to the materials and chiroptical requirements described above, there are additional chemical criteria that a successful dopant must satisfy. The barrier to racemization for the chiral dopant must be sufficiently high in the ground state so that it will not spontaneously racemize in the liquid crystalline medium, but sufficiently low in the electronically excited state to insure a large quantum yield for photoracemization (Φ_{RAC}). Additionally, the dopant must be photochemically stable. That is, irradiation cannot result in its destruction, but only its conversion from one enantiomer to the other.

Previously we reported the examination of 2,2′-ethano-bridged-*m*-terphenyl derivatives,[6] cyclic binaphthol-containing compounds,[7] and axially chiral (arylmethylene)cycloalkanes[5] as possible dopants. Herein we describe the synthesis and characterization of a series of optically active 1-benzylidenetribenzocycloheptatrienes (see Chart I). These compounds do not racemize thermally with an easily measurable rate at temperatures below 100 °C, but they do photoracemize with high efficiency when irradiated with UV light. They are photochemically stable and, with appropriate substitution, they have sufficiently large β_M values. However, the g_λ values we measure for these compounds are too small to induce an easily detectable cholesteric phase at the photostationary state when they are irradiated with circularly polarized light.

Results

(1) Synthesis and Characterization of Optically Active 1-Benzylidenetribenzocycloheptatrienes 1–5. Bergmann and Klein[8] reported the synthesis of 1 by the reaction of tribenzocyclohepta-2,4,6-triene-1-one with benzylmagnesium chloride. They measured its UV absorption spectrum and examined some of its other properties. Later, Tochtermann[9] and his co-workers prepared

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(1) Yoshizawa, T. *Adv. Biochem.* **1984**, *17*, 5.

(2) There have been previous attempts to employ liquid crystals as amplifiers of photochemical reactions: (a) Kreysig, D.; Stumpe, J. In *Selected Topics in Liquid Crystal Research*; Koswig, H. D., Ed.; Verlag: Berlin, 1990; p 69. (b) Haas, W.; Adams, J.; Wysocki, J. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 371. (c) Sackman, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088. (d) Kurihara, S.; Ikeda, T.; Sasaki, T.; Kim, H.-B.; Tazuke, S. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 251. (e) Gibbons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* **1991**, *351*, 49. (f) Ikeda, T.; Asamu, Z.; Sasaki, T.; Ichimura, K.; Tazoke, H.; Fukuda, A.; Skarp, K. A. W. *Mol. Cryst. Liq. Cryst.* **1992**, *225*, 67.

(3) Rau, H. *Chem. Rev.* **1983**, *83*, 535.

(4) Ruxer, J. M.; Solladie, G.; Candau, S. *Mol. Cryst. Liq. Cryst.* **1978**, *41*, 109.

(5) Lemieux, R. P.; Schuster, G. B. *J. Org. Chem.* **1993**, *58*, 100.

(6) Udayakumar, B. S.; Schuster, G. B. *J. Org. Chem.* **1992**, *57*, 348.

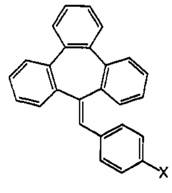
(7) Zhang, M. B.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063.

(8) Bergmann, E. D.; Klein, J. *J. Org. Chem.* **1958**, *23*, 512.

(9) Tochtermann, W.; Kuppers, H.; Franke, C. *Chem. Ber.* **1968**, *101*, 3808.

0022-3263/93/1958-4165$04.00/0

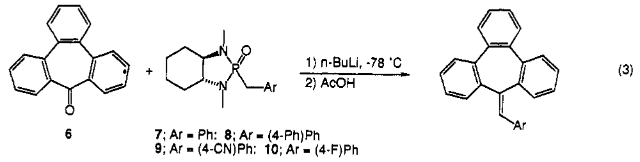
Chart I



1; X = H: 2; X = Ph: 3; X = CN:
4; X = F: 5; X = COCH$_3$

and studied optically active derivatives of methylenetribenzocycloheptatrienes by classical resolution of the vinyl carboxylic acid as its brucine salt. They examined the thermal racemization and found a barrier to isomerization ($\Delta G^{\ddagger}$) of 31 kcal/mol at 139 °C. This result indicates that thermal racemization of the tribenzocycloheptatriene ring will be slow under the irradiation conditions designed for the dopant in a liquid crystalline medium. There have been no reports of the direct asymmetric synthesis of 1 or any of its analogs and there were no quantitative measurements of the chiroptical properties of these compounds before this work.

The syntheses of compounds 1–4 follow from the adaptation of the Horner–Emmons reaction introduced by Hanessian for the preparation of optically active olefins.[10] The reaction sequence is illustrated in eq 3, and the details of the reactions are presented in the Experimental Section. Benzylidenecycloheptatriene 5 was prepared by reaction of 3 with methyllithium. The optical purities of 1 and 4 were determined to 72 and 5%, respectively, by analysis of their ^{1}H NMR spectra in the presence of chiral shift reagents Ag(fod) and either Eu(hfc)$_3$ or Yb(hfc)$_3$. The optical purity of 2 was determined to be 47% by chromatographic analysis on a WHELK-01 chiral HPLC column.[11] Unfortunately, we were unable to separate the enantiomers of 3 and 5 by HPLC, and their ^{1}H NMR spectra in the presence of chiral shift reagents were unresolved. We determined the optical purity of these compounds to be 92% by reduction of the methyl ketone group of 5 (which was derived from 3) to an ethyl group followed by analysis of the ethylbenzene derivative by NMR spectroscopy in the presence of chiral shift reagents.



6

7; Ar = Ph: 8; Ar = (4-Ph)Ph
9; Ar = (4-CN)Ph: 10; Ar = (4-F)Ph

(3)

(2) Absorption and Circular Dichroism Spectra of 1–5. One of the critical requirements for successful development of the dopants described in the Introduction is that they have g_λ values sufficiently large to induce a detectable cholesteric liquid crystal phase at the photostationary state when irradiated with circularly polarized light. The value of g_λ is obtained by measurement of both the absorption and circular dichroism spectra of compounds of known optical purity.

Figure 1 shows the absorption and circular dichroism spectra of compounds 1 and 5. Benzylidenecycloheptatriene 1 shows apparent maxima in its UV spectrum at 285 and 240 nm. Similarly, its circular dichroism spectrum shows a positive maximum at ca. 291 nm and a negative maximum at 243 nm. The values of g_λ calculated from these spectra are reported in Table I. The maximum value for this parameter (g_{243}) is 1.7 × 10^{-3} which corresponds to an ee$_{\text{MAX}}$ at the photostationary state of 0.085%. It is well known that g_λ values for carbonyl chromophores are sometimes very large because their nπ^* transitions are magnetic dipole allowed and electric dipole forbidden.[12] However, for compound 5 the intense $\pi\pi^*$ transition overlaps with the weaker nπ^* absorption and the maximum value of g (g_{375}) is only 1.6 × 10^{-3}. The UV and circular dichroism data for the other compounds investigated are reported in Table I. The maximum value for g_λ we obtain is 2.2 × 10^{-3} for 4.

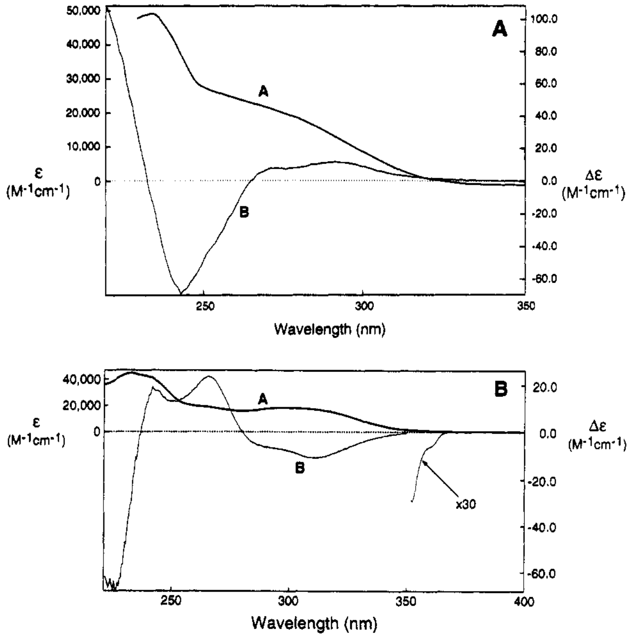


Figure 1. Panel A: Absorption (A, 2.8 × 10^{-5} M) and circular dichroism spectra (B, 3.0 × 10^{-4} M) of 1 in cyclohexane solution. Panel B: Absorption (A, 2.6 × 10^{-5} M) and circular dichroism spectra (B, 6.4 × 10^{-4} M) of 5 in cyclohexane solution.

Table I. Spectroscopic Data and Materials Properties

compound	$[\alpha]_D$,[a] deg	λ, nm (log ε, M^{-1} cm^{-1})	g_λ[a] × 10^4 (λ, nm)	β_M,[a] μm^{-1}
1	+380	237 (4.68) 300 (3.95)	17 (243) 9.0 (291)	7.8
2	−670	237 (4.66) 300 (4.44) 350 (3.18)	10 (256) 3.8 (303)	46
3	−590	222 (4.77) 287 (4.39)	4.6 (243) 5.8 (252) 10 (266) 3.2 (310)	*b*
4	+440	234 (4.75) 300 (4.03)	22 (243) 13 (291)	*b*
5	−650	300 (4.25) 353 (2.94)	5.5 (353) 16 (375)	10

[a] Values are corrected to 100% ee based on known optical purities. [b] Not determined.

(3) Investigation of Photoracemization and Photostability of 1–5 in Isotropic Solution. The photo-

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[10] Hannessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754. Hanessian, S.; Bennani, Y. L.; Delorme, D. *Tetrahedron Lett.* **1990**, *31*, 6461. Hanessian, S.; Beaudoin, S. *Tetrahedron Lett.* **1992**, *33*, 4576.

[11] This column is available commercially from Regis Corp.

[12] Schippers, P. H.; Dekkers, H. P. J. M. *J. Am. Chem. Soc.* **1983**, *105*, 79.

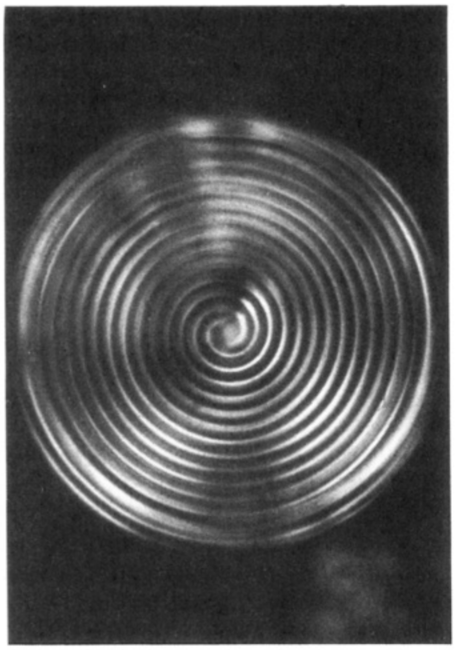

Figure 2. A single droplet of ZLI-1167 containing (+)-1 (C = 0.036) suspended in glycerol viewed at 400× magnification between crossed polarizers at room temperature. The distance between adjacent arms of the spiral is 2.6 μm.

stability of compounds 1–5 was determined relative to their rates for photoracemization since this ratio will determine their suitability for use as dopants. To determine the rates of photoracemization, N_2-purged cyclohexane solutions (10^{-3} M, 3 mL) of these compounds were irradiated at 300 nm in a Rayonet photochemical reactor at ambient temperature. The extent of their photoracemization was monitored by measuring the optical rotation of the samples. In all cases, complete racemization was obtained after 2 min, or less, of irradiation.

The photostability of compounds 1–5 was determined by irradiating them in cyclohexane solutions under identical conditions to the photoracemization experiment and monitoring the progress of the reaction by gas chromatography. The samples were irradiated for 1.5 h with no measurable decrease in their concentration or the appearance of any other compounds in the gas chromatographic trace. From these observations we conclude that the rate of photoracemization is at least 500 times greater than the rate of photodestruction for these benzylidenecycloheptatrienes.

(4) Determination of β_M and Photoracemization in Liquid Crystalline Media. The helical twisting powers (β_M) of compounds **1**, **2**, and **5** were determined by the droplet method[13] in the nematic liquid crystalline material ZLI-1167 (a mixture of 4-*n*-alkyl-4-cyano-1,1′-bicyclohexyls). Figure 2 shows a droplet of ZLI-1167 containing (+)-**1** viewed microscopically in glycerol between crossed polarizers at 400× magnification. The pitch of the liquid crystal phase is twice the distance between adjacent spirals. This experiment yields a value for β_M for **1** of 7.8 μm^{-1}. These data are reported in Table I. The pitch of the liquid crystal droplet did not change after it was heated at 80 °C for 1 h, indicating that **1** does not racemize thermally under these conditions. Interestingly, β_M for **2**, which contains a biphenylyl group, is 46 μm^{-1} nearly 6 times larger than that for **1**. It is generally the case that the more "similar" in structure a dopant is to that of the liquid crystalline host material, the greater is the value of β_M.[14] This seems to be true, too, for these compounds since the biphenylyl group of **2** is more similar to the bicyclohexyl group of ZLI-1167 than is the phenyl group of **1**.

The observation that compounds **1**–**5** photoracemize in fluid solution is not a guarantee that they will racemize in more viscous and anisotropic liquid crystalline media. We examined the irradiation of optically active samples of **1** in ZLI-1167 to insure that racemization occurs. A 2 mol %, air-saturated solution of (+)-**1** in ZLI-1167 constrained between two quartz slides viewed microscopically between crossed polarizers shows a typical cholesteric texture. When this solution is irradiated at 300 nm for ca. 1 min, the texture observed microscopically changes to that of a typical nematic liquid crystalline phase.[15] Similar experiments give the same result for the other optically active benzylidenecycloheptatrienes. Thus the photoracemization of these compounds appears to be efficient in both liquid crystalline media and in fluid solution.

Discussion

The chemical and materials properties of the benzylidenecycloheptatrienes investigated in this work provide insight into their application as possible dopants and expands our view of photoisomerization behavior of arylmethylene excited states.

The syntheses of optically active compounds **1**–**4** proceed satisfactorily by application of the Hanessian asymmetric olefination procedure. The case of **4** requires brief comment because the ee obtained in this instance is ca. 10 times lower than it is for the other examples reported. As described in the Experimental Section, the syntheses of optically active **1** and **4** were carried out in a similar manner to the other cases reported, as far as we could determine. However, this reaction was performed only once and we suspect some undetected error in operation may be the cause of the low ee obtained. Thus, there is likely no general principle revealed by this atypical result.

The photochemical properties of the benzylidenecycloheptatrienes are easily related to those of other arylethylenes such as the stilbenes and tetraphenylethylene. These olefins have been probed theoretically and experimentally by steady-state and time-resolved spectroscopic methods.[16] The seemingly simple geometric isomerization reaction of these aryl-substituted ethylenic systems has been shown to involve complex motions on the excited state potential energy surface proceeding through a series of structurally distinct states. The number and specific nature of these excited states is not certainly defined in all cases, but normally it appears that at least three states are involved.[17] Excitation leads to the vertical (Franck–

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[13] Seuron, P.; Solladie, G. *Mol. Cryst. Liq. Cryst.* **1979**, *56*, 1. Candau, S.; LeRoy, P.; Debeauvais, F. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 283.

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[15] Hartshore, N. H. *The Microscopy of Liquid Crystals*; Microscope Publications Ltd.: London, 1974. Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

[16] (a) Saltiel, J.; Sun, Y.-P. In *Photochromism: Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (b) Pederson, S.; Banares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 8801. (c) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 13. (d) Schilling, C. L.; Hilinsky, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 2296.

[17] Zimmt, M. B. *Chem. Phys. Lett.* **1989**, *160*, 564. Morais, J.; Ma, J.; Zimmt, M. B. *J. Phys. Chem.* **1991**, *95*, 3885. Ma, J.; Zimmt, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 9723.

Condon) singlet state, torsional relaxation about the aryl–ethylenic carbon bond gives a relaxed, sometimes emissive, excited state, and rotation around the ethylenic carbon–carbon bond leads to formation of the nonemissive perpendicular ("phantom") excited state. Internal conversion of the perpendicular excited state to the perpendicular ground state results in net isomerization. In the present case, isomerization does not cause interconversion of geometric isomers but results in photoracemization. Although we did not carry out a detailed photophysical analysis of compounds **1**–**5**, the thorough investigation of a related system has been recently reported and the basic principles governing the reaction appear to be the same for these systems as they are for other arylethylenes.[18] Most significantly, Φ_{RAC} in these compounds is large and there is no detectable photodestruction. These properties are satisfactory for the planned utilization of benzylidenecycloheptatrienes as dopants in liquid crystalline media.

A difficulty in the application of benzylidenecycloheptatrienes as dopants arises in their chiroptical properties. The data reported in Table I shows that β_M has a maximum value for **2**. Application of eqs 1 and 2, with an estimated ee for **2** at the photostationary state of 5×10^{-2}% (calculated from the g_λ value reported in Table I) reveals that the concentration (C) of **2** required to give a pitch of 100 μm is 0.44. This means that a minimum of 44% of the liquid crystalline phase must be composed of **2** in order that irradiation with circularly polarized light will convert the nematic phase containing racemic **2** to a detectable cholesteric form. Although, in principle, it may be possible to prepare such a liquid crystalline material, it is unlikely to have general utility.

Experimental Section

General. NMR spectroscopic data were recorded on a Varian XL 200 (200 MHz ^{1}H, 50 MHz ^{13}C NMR) instrument. UV absorption spectra were measured with a Perkin-Elmer 552 spectrophotometer. Low-resolution mass spectra were recorded on a Varian-MAT CH-5 mass spectrometer (70 eV). Optical rotations were measured on a JASCO DIP-360 digital polarimeter at room temperature using the sodium D line. Circular dichroism spectra were recorded on a SPEX CD VI (Jobin-Yvon, France) spectrometer in cyclohexane solution. A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC-MS analyses which were performed at 70 eV with 0.25 mm × 12 m HP-1 capillary column programmed at 150 °C for 3 min and then 250 °C at the rate of 15 °C min^{-1}. A Hewlett-Packard 5890 GC equipped with a flame ionization detector and an HP 3390A electronic integrating recorder was used for analytical separations. GC analyses were performed with 0.53 mm × 10 m HP-1 column. A Fisher Micromaster polarizing microscope equipped with Mettler FP 82 hot stage was used for microscopic analyses. Melting points are uncorrected. Elemental analyses were performed by the Microanalytical laboratory of the University of Illinois.

Determination of β_M Values. A 0.5-mg portion of (+)-**1** was added to 11.0 mg of ZLI-1167 (E. Merck). A homogeneous solution was prepared by repeatedly heating the mixture to 80 °C with stirring and then cooling to room temperature. Examination by differential scanning calorimetry revealed the following phase sequence: (heating, 10 °C/min) K; 8.1 S_1; 19.6 S_2; 29.5 N; 79.5 I: (cooling, 10 °C/min) I; 78.2 N; 27.9 S_2. A small droplet of the solution was mounted on a glass slide and viewed microscopically through crossed polarizers as the temperature was reduced from 80 °C. At 72.9 °C, small domains appeared and at 65.3 °C the solution took on the "oily streak" texture characteristic of a cholesteric phase which persisted to room temperature. An additional portion of the sample was dispersed in glycerol and the disclination pattern was recorded photographically, see Figure 2, to reveal a pitch of 5.2 μm.

Synthesis. The following compounds were prepared following literature procedures and were shown to have expected physical and spectral properties: (±)-1-Benzylidene-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (**1**);[8] tribenzo[*a,c,e*]cycloheptatrien-1-one (**6**);[9] diethyl [(4-cyanophenyl)methyl]phosphonate;[19] diethyl [(4-fluorophenyl)methyl]phosphonate,[20] (3a*R*,7a*R*)-2-benzyl-3a,4,5,6,7,7a-hexahydro-1,3-dimethyl-1,3,2-benzodiazaphosphole 2-oxide.[10]

Standard workup procedures for reactions typically involved dilution with ether (or CH_2Cl_2) and multiple extractions with water (occasionally with dilute acid or base as required), washing of the organic layer with a saturated NaCl solution to reduce its water content, drying over solid desiccant (usually $MgSO_4$), and, finally, evaporation of the solvent.

(+)-1-Benzylidene-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (1). To 395 mg (1.42 mmol) of (phenylmethyl)phosphonamide in 6 mL of THF was added 0.87 mL (1.36 mmol) of *n*-BuLi (1.57 M solution in hexanes, Aldrich) at −78 °C, with stirring under N_2. After 30 min of stirring, 350 mg (1.36 mmol) of tribenzocycloheptatrienone (**6**) in 2 mL of THF was added dropwise through a cannula, and the reaction mixture was stirred at that temperature for an additional 1 h. The reaction mixture was quenched with 0.6 mL of glacial acetic acid and slowly warmed to rt over a period of 1 h. The standard workup followed by column chromatography (silica gel, with 15% CH_2Cl_2 in hexanes as eluent) gave 110 mg (25% yield, 72% ee) of **1**: mp 70–90 °C; ^{1}H NMR ($CDCl_3$) δ 6.56 (s, 1H, benzylic), 7.00–7.78 (m, 17H, aromatic); ^{13}C NMR ($CDCl_3$) δ 126.0, 126.8, 127.2, 127.5, 127.5, 127.9, 127.9, 128.8, 129.0, 129.2, 129.6, 129.9, 130.4, 136.4, 137.3, 137.7, 138.7, 138.8, 142.2, 142.3, 146.3; GC-MS, *m/z* (rel inten) 330 (M^+, 100), 329 (29), 327 (16), 252 (20), 226 (6), 165 (10), 163 (12), 156 (13); UV (C_6H_{12}) λ_{max} 237 (log ϵ 4.68), 254 (4.44), 300 (3.95); CD (C_6H_{12}) λ_{max} 243 ($\Delta\epsilon$ = −71), 291 (11.6). Anal. Calcd for $C_{26}H_{18}$: C, 94.50; H, 5.49. Found: C, 94.56; H, 5.53.

(−)-1-(*p*-Biphenylylmethylene)-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (2). To 330 mg (0.93 mmol) (*p*-biphenylylmethyl)phosphonamide in 4.5 mL of dry THF at −78 °C was added dropwise 480 μL (0.75 mmol) of *n*-BuLi in hexanes. The mixture was stirred for 30 min and then a THF solution (1 mL) containing 190 mg (0.75 mmol) of tribenzocycloheptatrienone **6** was added dropwise. Stirring was continued for 1 h, and then the reaction was quenched with 0.60 mL of glacial HOAc. The solution was warmed to room temperature and the standard workup followed by column chromatography on silica gel with 20% CH_2Cl_2 in hexanes as eluent gave 290 mg (95% yield, 47% ee) of **2**: mp 82–125 °C; ^{1}H NMR ($CDCl_3$) δ 6.59 (s, 1H, benzylidene), 7.10–7.80 (m, 21H, aromatic); ^{13}C NMR ($CDCl_3$) δ 126.0, 126.5, 126.8, 127.2, 127.3, 127.5, 127.6, 128.0, 128.6, 128.6, 128.9, 129.6, 129.6, 129.9, 130.4, 135.5, 137.4, 137.7, 138.74, 138.85, 139.4, 140.5, 142.3, 142.5, 146.4; low-resolution MS, *m/z* (rel inten) 406 (M^+, 100), 405 (7), 329 (4), 327 (6), 252 (12), 250 (3), 203 (5), 43 (25); UV (cyclohexane) λ_{max} 210 (log ϵ 4.72), 236 (4.67), 300 (4.47); CD (cyclohexane) λ_{max} 256 ($\Delta\epsilon$ 24.5), 303 (−10.5). Anal. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.45. Found: C, 94.54; H, 5.44.

(−)-1-(*p*-Cyanobenzylidene)-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (3). A dry THF solution (8 mL) containing 350 mg (1.2 mmol) of (*p*-cyanobenzyl)phosphonamide was treated with 700 μL of a *n*-hexane solution of *n*-BuLi (1.17 mmol) at −78 °C. The reaction mixture was stirred for 0.5 h and then a THF solution (2 mL) containing 200 mg (0.78 mmol) of tribenzocycloheptatrienone **6** was added. After 1 h at −78 °C, the reaction mixture was treated with 0.6 mL of glacial HOAc and warmed to room temperature. After 20 min at room temperature, the mixture was cooled to 0 °C and subjected to the standard workup followed by chromatography on silica gel with toluene as eluent to give 230 mg (84% yield, 92% ee) of (−)-**3**: mp 102–110 °C; CD (cyclohexane) λ_{max} 243 ($\Delta\epsilon$ 28 M^{-1} cm^{-1}), 252 (18.3), 266 (30.0),

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[20] Ernst, L. *Organic Magnetic Resonance* **1977**, *9*, 35.

310 (−6.13). Anal. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82; N, 3.94. Found: C, 91.18; H, 4.87; N, 3.87.

(+)-**3**: mp 199–200 °C; ^{1}H NMR ($CDCl_3$) δ 6.57 (s, 1H, benzylidene), 7.02–7.77 (m, 16H, aromatic); ^{13}C NMR ($CDCl_3$) δ 110.0, 116.4, 125.7, 126.8, 127.3, 127.7, 127.78, 128, 128.1, 128.1, 128.2, 129, 129.6, 129.8, 129.9, 130.5, 131.7, 137, 137.6, 138.4, 138.4, 141.2, 145.4, 146.2; UV (cyclohexane) λ_{max} 222 (log ε 4.77), 258 (4.46), 287 (4.39); GC-MS, *m/z* (rel inten) 355 (M^+, 100), 354 (27), 327 (9), 252 (21), 250 (9), 226 (6), 177 (8), 176 (9), 162 (10).

(+)-1-(*p*-Fluorobenzylidene)-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (4). To 345 mg (1.17 mmol) of (*p*-fluorobenzyl)phosphonamide in 8 mL of dry THF at −78 °C was added 700 μL (1.17 mmol) of *n*-BuLi in *n*-hexanes. After stirring at −78 °C for 0.5 h, the solution was treated with 2 mL of a THF solution containing 200 mg (0.78 mmol) of tribenzocycloheptatrienone **6**. The reaction mixture was maintained at that temperature for 1 h and then treated with 0.6 mL of glacial HOAc, warmed to room temperature, stirred for 20 min, and cooled to 0 °C prior to the standard workup. Silica gel chromatography with toluene as eluent gave 184 mg (68% yield, 5.1% ee) of **4**: mp 156 °C; CD λ_{max} 242 (Δε = −96), 291 (20.7).

(±)-**4**: mp 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 6.53 (s, 1H, benzylic), 6.78–7.75 (m, 16H, aromatic); ^{13}C NMR ($CDCl_3$) δ 114.7, 115.1, 126, 127.2, 127.5, 127.6, 127.7, 127.8, 128.0, 128.9, 129.7, 129.9, 130.4, 130.7, 130.8, 135.9, 137.4, 138.8, 142.0; GC-MS *m/z* (rel inten) 348 (M^+, 100), 347 (20), 333 (7), 331 (5), 326 (6), 252 (9), 177 (2), 163 (2); UV (cyclohexane) λ_{max} 234 (log ε 4.75), 274 (4.53), 291 (4.21), 300 (4.04). Anal. Calcd for $C_{26}H_{17}F$: C, 89.63; H, 4.92. Found: C, 89.75; H, 4.92.

(−)-(*p*-Acetylbenzylidene)-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene (5). To 25 mg (0.07 mmol) of (−)-**3** in 1 mL of dry ether was added 75 μL (0.10 mmol) of a methyllithium solution in hexane at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The excess methyllithium was destroyed by addition of 1 mL of saturated NH_4Cl at 0 °C. After standard workup, preparative TLC (silica gel, using CH_2Cl_2) gave 27 mg (73%, 92% ee) of **5**: mp 165–166 °C; ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H, methyl), 6.62 (s, 1H, benzylidene), 7.10–7.16 (m, 3H, aromatic), 7.19–7.52 (m, 7H, aromatic), 7.60–7.80 (m, 6H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.4, 125.8, 127.0, 127.6, 127.6, 127.8, 127.9, 128, 128.9, 129.2, 129.7, 129.9, 130.4, 135.1, 137.1, 137.6, 138.5, 138.5, 141.4, 141.7, 145.1, 145.7, 197.5; UV (cyclohexane) λ_{max} 225 (log ε 4.64), 254 (4.28), 300 (4.25); CD (cyclohexane) λ_{max} 242 (Δε = 20), 252 (13.8), 266 (23.0), 289 (−6.32), 310 (−10.9), 375 (0.06).

(*p*-Ethylbenzylidene)-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-triene. To 97 mg (0.73 mmol) of aluminum chloride dissolved in 5 mL of ether was added 13.8 mg (0.36 mmol) of lithium aluminum hydride. A 5-mL portion of an ether solution of 13.6 mg (0.036 mmol) of **5** was added dropwise, and the reaction mixture was heated at reflux for 30 min. After cooling, the mixture was diluted with 15 mL of ether, and standard workup gave 95 mg (92% ee): ^{1}H NMR ($CDCl_3$) δ 1.13 (t, 3H, *J* = 7.05 Hz, methyl), 2.52 (q, 2H, *J* = 7.05 Hz, methylene), 6.52 (s, 1H, benzylidene), 6.94 (s, 4H, aromatic), 7.18–7.21 (m, 2H, aromatic), 7.28–7.48 (m, 6H, aromatic), 7.52–7.72 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.3, 28.5, 126.0, 127.3, 127.4, 127.5, 127.9, 127.9, 128.84, 128.9, 129.2, 129.3, 129.6, 129.9, 130.3, 133.8, 137.4, 133.8, 138.8, 138.9, 141.4, 142.5, 143.0, 146.6; MS-EI *m/z* (rel inten) 358 (M^+, 100), 356 (14), 343 (28), 329 (14), 328 (13), 327 (14), 326 (11), 252 (12), 163 (9), 157 (7), 91 (7); HR-EI calcd for $C_{28}H_{22}$ 358.1721, found 358.1725.

(3a*R*,7a*R*)-2-(*p*-cyanobenzyl)-3a,4,5,6,7,7a-hexahydro-1,3-dimethyl-1,3,2-benzodiazaphosphole 2-Oxide (9). A solution of 4.96 g (19.6 mmol) of diethyl (*p*-cyanobenzyl)phosphonate in 5.6 mL (42.6 mmol) of TMSBr was stirred at rt for 1 h under N_2. The volatile products were removed under reduced pressure. The residue was dissolved in 25 mL of dry CH_2Cl_2 and treated with 12 drops of DMF and 5.60 mL (64 mmol) of oxalyl chloride. The reaction mixture was stirred at room temperature overnight. Evaporation of volatile products gave 3.4 g (74% yield) of (*p*-cyanobenzyl)phosphonyl dichloride, which was carried to the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 3.96 (d, 2H, J_{PH} 21.7 Hz, benzyl), 7.39–7.48 (m, 2H, aromatic), 7.59–7.68 (m, 2H, aromatic).

A 100-mL portion of a 1:1 (volume) mixture of CH_3CN/C_6H_6 containing 3.4 g (14.5 mmol) of (*p*-cyanobenzyl)phosphonyl dichloride was added dropwise to a solution of 1.88 g (13.2 mmol) *N,N'*-dimethyl-1,2-diaminocyclohexane[6] and 2.67 g (26 mmol) of Et_3N in 50 mL of dry benzene at 0 °C. The reaction mixture was warmed to room temperature, stirred for 24 h, and then filtered. The precipitate was washed with 40 mL of EtOAc, and the combined filtrate was dried over anhyd Na_2SO_4. Evaporation of the solvent followed by column chromatography (silica gel 1:9 $MeOH/CHCl_3$ as eluent) gave 3.0 g (69% yield) of **9** as a light yellow solid: mp 184–185 °C; $[\alpha]_D$ = −132° (*c* 1.61, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.79–1.35 (m, 4H, cyclohexane), 1.74–2.15 (m, 5H, cyclohexane and *C*H[N]), 2.32 (d, 3H, J_{CP} 10.4 Hz, NCH_3), 2.54 (d, 3 H, J_{CP} 10.4 Hz, NCH_3), 2.60–2.68 (m, 1H, *CH*N), 2.94–3.42 (m, 2H, CH_2Ph), 7.32–7.40 (m, 2H, aromatic), 7.56 (d, 2H, *J* 8.33 Hz, aromatic); HR-EI calcd for $C_{16}H_{22}N_3PO$ 303.1501, found 303.1500.

A similar procedure was followed for the preparation of **10**: (24%; mp 113–114 °C; ^{1}H NMR ($CDCl_3$) δ 0.82–1.40 (m, 4H, cyclohexane), 1.71–2.10 (m, 5H, cyclohexane and *CH*N), 2.40 (d, 3H, J_{PH} 10.41 Hz, NCH_3), 2.58 (d, 3H, J_{PH} 10.41 Hz, NCH_3), 2.62–2.72 (m, 1H, *CH*N), 2.94–3.37 (m, 2H, CH_2Ph), 6.94–7.03 (t, 2H, *J* 8.33 Hz, aromatic), 7.19–7.27 (m, 2H, aromatic); MS *m/z* (rel inten) 296 (M^+, 14), 187 (100), 169 (3), 110 (13), 109 (17), 107 (3), 83 (6), 68 (4); HR-EI calcd for $C_{15}H_{22}FN_2OP$ 296.1453, found 296.1465. Anal. Calcd for $C_{15}H_{22}FN_2OP$: C, 60.79; H, 7.48; N, 9.45. Found: C, 60.81; H, 7.56; N, 9.38.

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Supplementary Material Available: Copies of NMR and mass spectra of the *p*-acetylbenzylidene (**5**) and *p*-ethylbenzylidene derivatives (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.