recrystallized three times from methanol. Di-α-cumyl hyponitrite was prepared from α-cumyl bromide and silver hyponitrite by the method of Kiefer and Traylor.[15]

Product Yields. Yields of acetophenone and α-cumyl alcohol from decomposition of di-cumyl peroxide and di-cumyl hyponitrite were determined by high-performance liquid chromatography using a Varian 5000 liquid chromatograph controlled by a Vista 401 chromatography data system. The chromatograph was equipped with a reverse-phase column, and the eluting solvent was a mixture of acetonitrile and water. The solvent initially contained 40% acetonitrile, and the percentage of this constituent was gradually increased to 100%.

Laser Flash photolysis. All experiments were carried out in deaerated samples contained in Suprasil cells made of 7 × 3 mm² rectangular tubing. A Molectron UV-24 nitrogen laser, delivering pulses at 337.1 nm, was used for excitation. The transient signals were initially recorded by a Tektronix 7912 transient digitizer and then transferred to a PDP-11/23 computer, which was also used to control the experiment, for data processing, as well as to provide suitable storage and hardcopy facilities. Further details have been reported elsewhere.[16]

Registry No. $(PhC(Me_2)O)_2$, 80-43-3; $PhC(Me_2)O\cdot$, 16812-36-5; H, 1333-74-0; cumene, 98-82-8; diphenylmethanol, 91-01-0; tetrahydrofuran, 109-99-9; cyclohexene, 110-83-8; 1-octene, 111-66-0; 1,3-cyclooctadiene, 1700-10-3; cyclohexane, 110-82-7; phenol, 108-95-2; di-α-cumyl hyponitrite, 21799-93-9; α-cumyl bromide, 3575-19-7; silver hyponitrite, 7784-04-5.

(15) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, 6163–6168.
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Electronic Absorption and Circular Dichroism Spectra of the Perturbed Coplanar *cis*-Diene Chromophore in Deuterium- and Methyl-Substituted 7,7-Dimethylbicyclo[4.1.1]octa-2,4-dienes

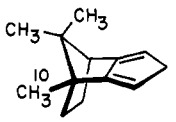
Alan R. Browne,[1a] Alex F. Drake,[1b] Francis R. Kearney,[1a] Stephen F. Mason,*[1b] and Leo A. Paquette*[1a]

Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and King's College, London WC2R 2LS, England. *Received February 10, 1983*

Abstract: The optically active monodeuterated 7,7-dimethylbicyclo[4.1.1]octa-2,4-dienes **6** and **8** have been prepared with known absolute configuration from (+)-nopinone. Access to their methyl congeners **7** and **9** has been achieved from (+)-α-pinene and (+)-nopinone, respectively. In **6** and **8**, the chirality is due solely to isotopic substitution. The contributions of the C–D and $C-CH_3$ groups to the observed absorption and circular dichroism spectra are analyzed. In particular, attention is directed to the planar *cis*-1,3-diene unit in **6–9**, the resultant zero dihedral angle between the C_2-C_3 and C_4-C_5 bonds at equilibrium, and the consequences of this unique fixed geometry.

The chiroptical properties of chiral, cisoid, *nonplanar* 1,3-dienes have been extensively studied over the years.[2] The early analyses suggested that the particular sign of the observed long-wavelength Cotton effects is controlled largely by the helicity of the inherently dissymetric skewed diene chromophore,[3] but subsequently chiroptical contributions by homoallylic and bis(homoallylic) substituents, both axial[4] and equatorial,[5] were found to be substantial.[6] Unfortunately, competing chirality contributions resulting from dihedral angle alterations in conformationally flexible systems can often lead to ambiguous results.[5]

In the present study, we give attention to planar, inflexible 1,3-diene systems whose chirality is dependent solely upon deuterium or methyl substitution at the α and β positions. Only recently has ^2H-induced perturbation of isolated[7] and homoconjugated carbon–carbon double bonds[8,9] been given some attention. No prior assessment appears to have been made of this theoretically interesting combination of structural features, although investigation of the more remotely perturbed "quasi-planar" dienes **1**[10] and **2**[11] has been recently completed.



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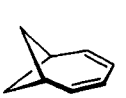
2

In order to isolate the effect of deuterium or methyl perturbation from other chiroptical influences generally associated with chiral molecules, it becomes highly desirable to deal with compounds that possess an achiral skeleton. In this manner, the chirality of the substrate is due solely to the substituent. This criterion is best met by ring systems endowed with axes or planes of symmetry, provided that all symmetry planes are destroyed upon substitution. We considered our purposes to be best served by the bicyclo[4.1.1]octa-2,4-diene framework (**3**), where strong interaction (β



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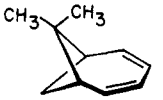

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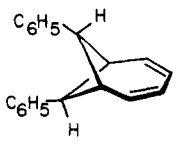

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(1) (a) The Ohio State University. (b) King's College.
(2) Lightner, D. A.; Bouman, T. D.; Gawroński, J. K.; Gawrońska, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314 and references cited therein.
(3) (a) Deen, R.; Jacobs, H. J. C. *Proc. K. Ned. Akad. Wet.* **1961**, *64*, 313. (b) Moscowitz, A.; Charney, E.; Weiss, U.; Ziffer, H. *J. Am. Chem. Soc.* **1961**, *83*, 4661. (c) Charney, E. *Tetrahedron* **1965**, *21*, 3127.
(4) Zushi, S.; Kodama, Y.; Fukuda, Y.; Nishihata, K.; Nishio, M.; Hirota, M.; Uzawa, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2113.
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(8) Paquette, L. A.; Kearney, F. R.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 5064.
(9) Lightner, D. A.; Gawroński, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 5749.
(10) Burgstahler, A. W.; Bodger, D. L.; Naik, N. C. *Tetrahedron* **1976**, *32*, 309.
(11) Sonney, J.-M.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 1034.

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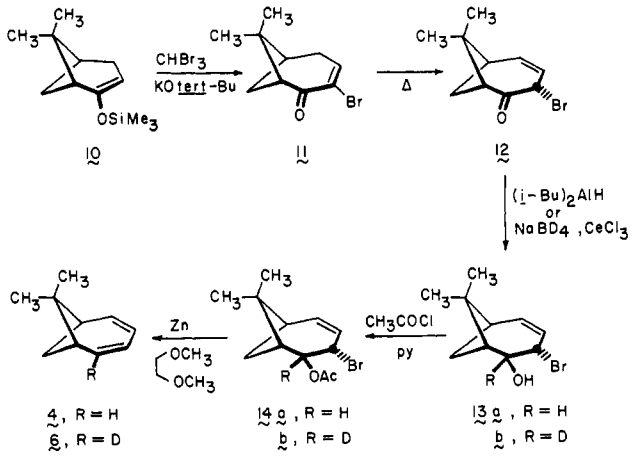
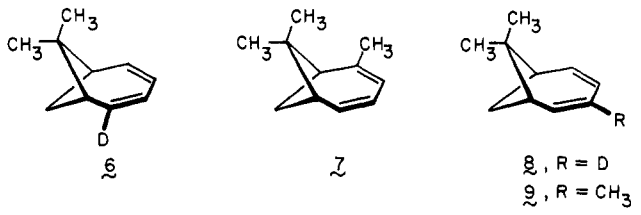
Scheme I



= −1.9 eV) is known to exist between the Walsh cyclobutane ring orbitals and π network.[12] For obvious practical reasons, it becomes necessary to reduce the C_{2v} symmetry of **3** to a more manageable C_s level as in **4**.[13] Any distortion arising from the added geminal methyl pair was considered to be negligible. Our selection of **4** was predicted upon the recent discovery by X-ray analysis that the only known crystalline bicyclo[4.1.1]octa-2,4-diene, **5**, possesses a rigidly fixed, planar diene moiety.[14]

For these reasons, we chose to prepare the four dienes **6–9** by methods that would allow for proper absolute configurational assignments and to elucidate their CD behavior.



Synthesis and Absolute Configurational Assignments. Consideration of appropriate, readily available, chiral pool sources suggested (+)-nopinone and (+)-α-pinene to be potentially useful if suitable ring expansion sequences could be developed. The absolute configurations of this bicyclic ketone[15] and hydrocarbon[16] are, of course, well-known, and these assignments are utilized for all formulas depicted herein.

Trimethylsilyl enol ether **10** was prepared from (+)-nopinone according to the general procedure devised by House[17] and treated with dibromocarbene[18] (Scheme I). The resulting dihalocyclopropane underwent spontaneous ring opening under the reaction conditions, perhaps because of high strain levels, to deliver enone **11**. Upon being warmed to 40 °C for several hours prior to distillation, **11** experienced isomerization to its β,γ-unsaturated isomer. This course of events is presumably driven by strain relief associated with the disengagement of three contiguous sp^2-hybridized carbon atoms. The configuration of the bromine-substituted carbon is based solely upon steric considerations. Following smooth reduction of **12** with diisobutylaluminum hydride (DIBAL-H), the bromohydrin was acetylated and reduced with zinc in dimethoxyethane solution. The known diene **4**[13] resulted.

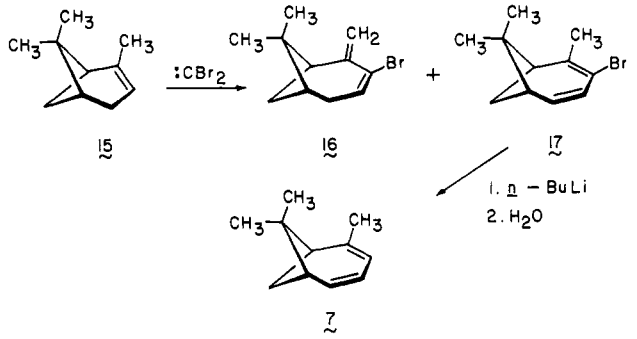
Since diisobutylaluminum deuteride is not readily available, we required another reducing agent that would not preferentially attack the bromine substituent in **12**. Sodium borohydride is known to reduce halides,[19] but the same reagent in the presence of cerous chloride is reputed to be selective for 1,2-enone reduction.[20] The latter phenomenon worked nicely to our advantage as the uncatalyzed reaction of **12** with $NaBH_4$ gave no **13a**, whereas $NaBD_4$ with added cerous chloride provided **13b** in 74% yield. The level of deuterium incorporation was ≥95% (NMR analysis), and the enantiomeric purity was determined to be 87% by ^{19}F and ^1H NMR studies on the (−)-phenyl α-methoxy-α-(trifluoromethyl)acetate (Mosher ester[21]). Acetylation and reductive elimination of **13b** as before afforded **6**, the optical rotation data for which are compiled in Table I.

Table I. Optical Rotation Data for 6–9 ($CHCl_3$ Solution)[a]

λ, nm	(1*S*)-6	(1*S*)-8	(1*R*)-7	(1*S*)-9
589	+2.6°	−1.4°	+26.4°	+0.7°
578	+3.6°	−1.4°	+27.7°	+1.0°
546	+3.2°	−1.6°	+32.8°	+2.2°
436	+5.3°	−9.3°	+66.8°	+15.4°
365	+8.9°	+9.3°	+162.6°	+88.5°

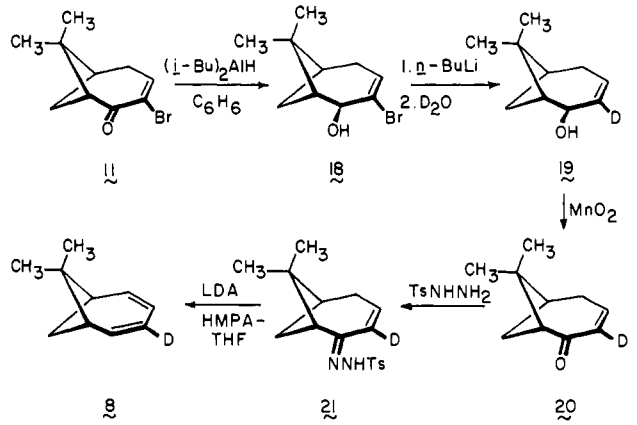
[a] All values have been properly corrected for enantiomeric purity.

Scheme II



To arrive at **7**, we relied on earlier reports that exposure of α-pinene (**15**) to dibromocarbene gives rise to a 4:1 mixture of exocyclic (**16**) and endocyclic (**17**) ring-expanded bromodienes[22] (Scheme II). Without separation, this pair of isomers was treated consecutively with *n*-butyllithium and water. Subsequent VPC purification led conveniently to the desired 2-methyl derivative.

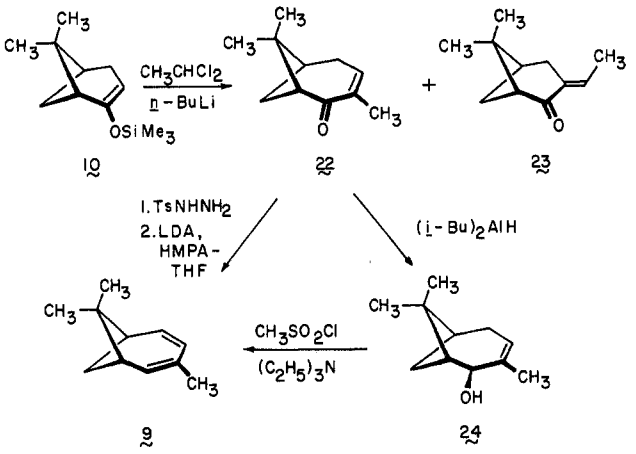
Scheme III



An expedient route to **8** originated with the DIBAL-H reduction of **11**, transmetalation within bromohydrin **18** by means of excess *n*-butyllithium,[23] and ultimate D_2O quench (Scheme III). The

(12) Gleiter, R.; Bischof, P.; Volz, W. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 8.
(13) Young, S. D.; Borden, W. T. *Tetrahedron Lett.* **1976**, 4019.
(14) Chasey, K. L.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 5262.
(15) Meinwald, J.; Gassman, P. G. *J. Am. Chem. Soc.* **1960**, *82*, 5445.
(16) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5491.
(17) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.
(18) Amice, P.; Blanco, L.; Conia, J.-M. *Synthesis* **1976**, 196.
(19) Bell, H. M.; Vanderslice, C. W.; Spehar, A. *J. Org. Chem.* **1969**, *34*, 3923.
(20) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2266.
(21) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(22) (a) Hatem, J.; Waegell, B. *Tetrahedron Lett.* **1971**, 2069. (b) Mehta, G.; Narang, S. C. *Ind. J. Chem.* **1972**, *10*, 1057.
(23) Paquette, L. A.; Lavrik, P. B.; Summerville, R. H. *J. Org. Chem.* **1977**, *42*, 2659.

Scheme IV



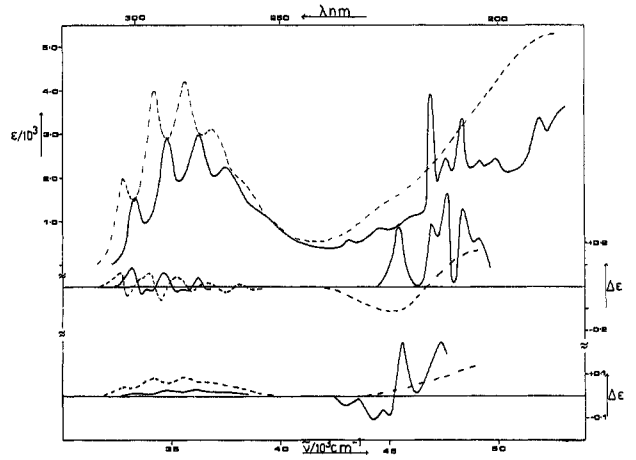


Figure 1. Absorption spectra of the 2- and 3-deuterio dienes **6** and **8** (top curves), and circular dichroism of **6** (middle curves) and **8** (bottom curves) in the gas phase (full line) and in 3-methylpentane solution (broken line).

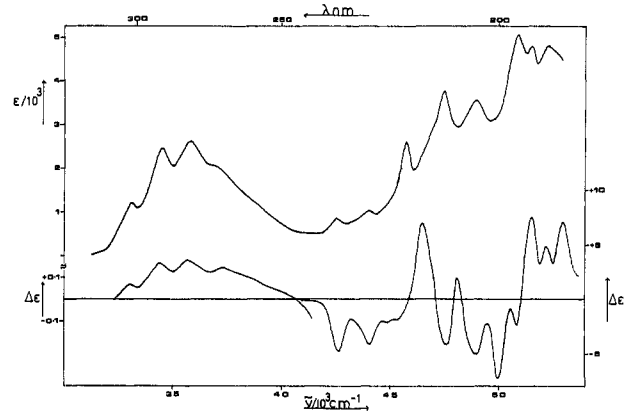


Figure 2. Absorption spectrum (upper curve) and circular dichroism (lower curve) of the 3-methyl diene **9** in the gas phase.

resulting deuterated (≥95% *d*) alcohol **19**, obtained as a beautifully crystalline solid, was rapidly and cleanly converted to **20** upon oxidation with activated manganese dioxide. Transformation of the derived tosylhydrazone into **8** was readily accomplished under modified Shapiro conditions.[24]

Condensation of **10** with methylchlorocarbene[25] led to the formation of nopinone, the bicyclo[4.1.1]oct-3-enone **22**, and ethylidenenopinone (**23**) (Scheme IV). Following separation by high-pressure liquid chromatography, **22** was successfully converted to **9** by two routes. DIBAL-H reduction provided **24** whose enantiomeric purity was determined to be 89% by conversion to the Mosher ester as before. Exposure of this alcohol to methanesulfonyl chloride and triethylamine in cold dichloromethane delivered the diene in unacceptably low (5%) yield. For this reason, it proved preferable to arrive at **9** by Shapiro degradation of the tosylhydrazone of **22**.

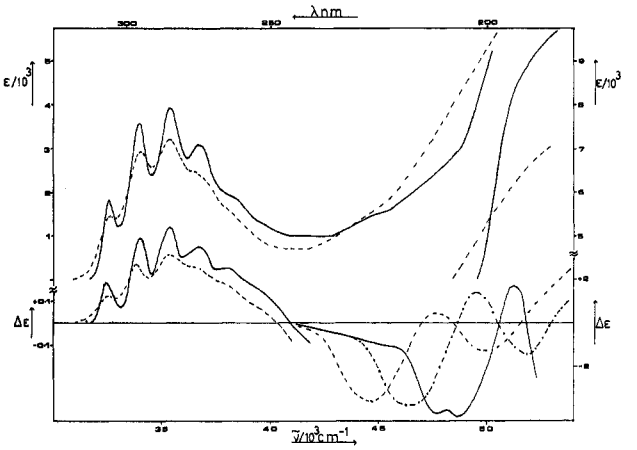


Figure 3. Absorption spectra (upper curves) and circular dichroism (lower curves) of the 3-methyl diene **9** in 3-methylpentane solution at −180 °C (full line), −100 °C (dash-dot line), and +20 °C (broken line).

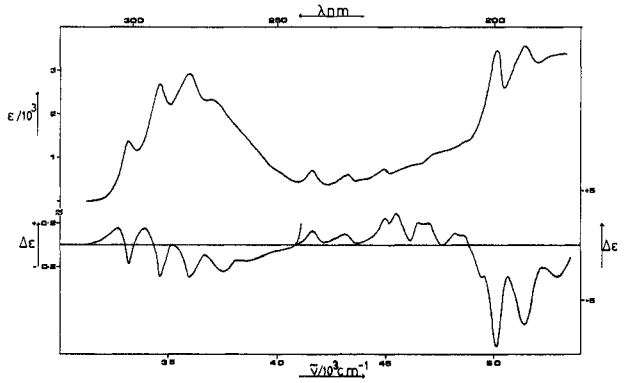


Figure 4. Absorption spectrum (upper curve) and circular dichroism (lower curve) of the 2-methyl diene **7** in the gas phase.

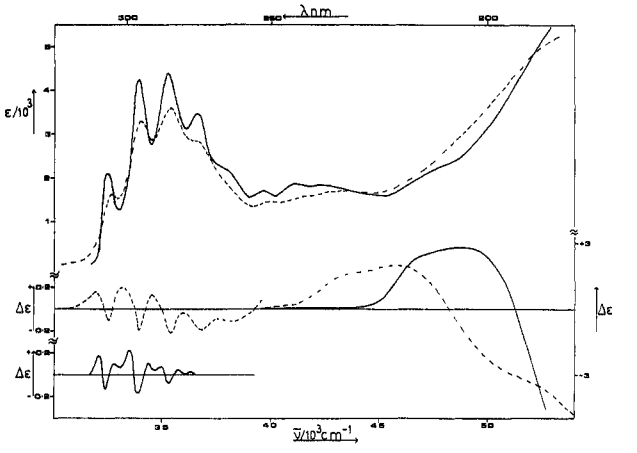


Figure 5. Absorption spectra (upper curves) and circular dichroism (lower curves) of the 2-methyl diene **7** in 3-methylpentane solution at −180 °C (full line) and at +20 °C (broken line).

Absorption and Circular Dichroism Spectra. The electronic absorption and CD spectra of the dienes **6–9** were measured with the instruments previously described.[26] The spectra of each diene in the gas phase and in 3-methylpentane solution were obtained

(24) Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405.
(25) Blanco, L.; Amice, P.; Conia, J.-M. *Synthesis* **1981**, 289.
(26) Drake, A. F.; Mason, S. F. *Tetrahedron* **1977**, *33*, 937.

at 20 °C over the 350–180-nm range, and the solution spectra of the dienes **7** and **9** were recorded additionally at −100 and −180 °C (Figures 1–5).

Over the range 330–250 nm of the lowest energy diene absorption due to the transition $\pi_2 \rightarrow \pi_3^*$, with the π-MOs numbers serially upward from the most bonding π-level, no major differences are observed between the gas phase and the solution spectra of a given diene, nor between the 20 and the −180 °C solution spectra of **7** and **9**. The $\pi_2 \rightarrow \pi_3^*$ band system of a given diene undergoes a small red shift and a minor increase in intensity on passing from the vapor phase to 3-methylpentane solution, as is expected for an electronic transition between molecular orbitals composed of valence-shell atomic orbitals, a N → V transition.[27] Both the red shift and the intensity enhancement derive from the polarization of the solvent molecules by the electric dipole moment of the $\pi_2 \rightarrow \pi_3^*$ transition in the diene solute.[28]

At shorter wavelengths, over the 250–180-nm range, the detailed vibrational structure of the gas-phase absorption and CD spectra is lost in the corresponding solution spectra. Generally, the CD bands are shifted to the blue, and in the cases of the dienes **7** and **9**, a further blue-shift of the CD band maxima results on cooling the solution from 20 to −100 °C and further to −180 °C. The blue shift of the CD band maxima leaves behind, however, a residual weak and broad CD absorption in the 45 000-cm^{-1} region (Figures 1–5).

Following the $\pi_2 \rightarrow \pi_3^*$ transition of the diene chromophore (N → V_1), two further π-valence-state transitions (N → V_2, V_3) are expected[27] at higher energy, arising from combinations of the orbital promotions, $\pi_2 \rightarrow \pi_4^*$ and $\pi_1 \rightarrow \pi_3^*$, which are degenerate in the zero order, together with Rydberg transitions (N → R). The Rydberg transitions are due to electronic promotions from the highest occupied diene orbital, π_2, to large, diffuse orbitals, outside the valence shell. The lowest lying Rydberg orbitals, in order of increasing energy, have 3s, 3p, and 3d character, and transitions to these orbitals from π_2 commonly overlap the higher energy valence transitions,[27] N → V_2, V_3. Owing to the large size of the Rydberg orbitals, their energies are raised and spread over a range of values by a change from the gas phase to solution, where the intermolecular attractions between the solvent molecules produce an effective internal pressure, which increases as the temperature of the solution is reduced.

The Rydberg transitions are prominent in the gas-phase spectra of the dienes studied, on account of their narrow bandwidths (≤500 cm^{-1}). The $\pi_2 \rightarrow$ 3s Rydberg promotion has an origin at 43 100 cm^{-1} for the deuterio dienes **6** and **8** with two members of a progression in 1500 cm^{-1}, the C=C stretching frequency in the excited state. The first-ionization potential of the diene **8**, IP(π_2) = 8.02 ± 0.02 eV from the UV photoelectron spectrum, and the Rydberg equation,[27,29]

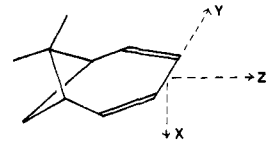
$$\bar{\nu}(\pi_2 \rightarrow nl) = \mathrm{IP}(\pi_2) - R/(n-\delta)^2 \qquad (1)$$

where the Rydberg, R = 109 737 cm^{-1}, give the quantum defect, δ 0.75, close to the corresponding value (0.72) estimated for cyclopentadiene.[29] The higher Rydberg transitions in the gas-phase spectra of the dienes **6** and **8**, $\pi_2 \rightarrow$ 3p, 3d, have origins at 46 900 and 51 900 cm^{-1}, respectively, giving the quantum defects δ 0.52 and 0.07, respectively, from eq 1. The particular values of the quantum defects estimated are consistent with the respective $\pi_2 \rightarrow$ 3s, 3p, 3d assignments, as is the division of the $\pi_2 \rightarrow$ 3p Rydberg band system into two progressions in the C=C stretching frequency in the upper state (1500 cm^{-1}), separated by 750 cm^{-1}, corresponding to the interval between the $3p_\pi$ and $3p_\sigma$ excited state[27] (Figure 1). The corresponding Rydberg transitions of the methyl-substituted dienes **7** and **9** in the gas-phase spectra lie at similar frequencies, with a red shift of some 1500 cm^{-1} in the case of **7** (Figures 2 and 4).

In the solution spectra of the dienes studied, the characteristic sharp vibrational structure of the Rydberg band system disappears, but the diffuse nature of the upper-state charge distribution is evident from the marked blue shift of the absorption produced by cooling the solution. The blue shift of the CD spectra 250–180 nm of **7** and **9** is particularly large, some 3000 cm^{-1} between 20 and −180 °C, indicating the N → R transitions contribute more to the optical activity in this region than the N → V_2, V_3 transitions, which are expected[27] to make the major contribution to the isotropic absorption (Figures 3 and 5).

It is notable that the CD absorption of the dienes **7** and **9** in the 250–180-nm region of the N → R, V_2, V_3 excitations is more than an order of magnitude larger than the corresponding CD in the 330–250-nm range of the N → V_1 transition (Figures 2–5). The Rydberg transitions significant for the relatively strong optical activity of the dienes **7** and **9** in the 250–180-nm region are probably $\pi_2 \rightarrow 3p_\sigma$, $3p_\pi$, which have a magnetic and an electric dipole moment, respectively. The two moments remain orthogonal in the C_{2v} coplanar *cis*-diene chromophore of **6**–**9** in their equilibrium nuclear configuration, and a perturbation reducing the chromophoric symmetry to C_2 or lower, removing the σ–π distinction, is required to give the two moments a nonvanishing scalar product, the rotational strength.

As noted above, early studies of the relationship between the optical activity of a chiral *cis*-1,3-diene and its stereochemistry were directed to the N → V_1 Cotton effect in dienes with a nonzero dihedral angle between the C_1–C_2 and C_3–C_4 bonds at equilibrium.[30-32] The diene helicity rule[33] resulting from these studies connects a positive $\pi_2 \rightarrow \pi_3^*$ CD absorption with a right-handed (P) chromophoric helicity or a corresponding negative CD with



a left-handed (M) helicity. Subsequently, allylic axial substituents to a cisoid diene were found to make $\pi_2 \rightarrow p_3^*$ CD contributions as significant as, or more important than, the chromophore helicity.[31,34] Thus **1**, with an essentially coplanar *cis*-diene chromophore, gives a $\pi_2 \rightarrow \pi_3^*$ CD of $\Delta\epsilon$ −0.55 at 240 nm, which is attributed to the polarization of the allylic bond to the 10-methyl group.[10] Whereas the 10-methyl group of **1** is displaced from the chromophore plane at equilibrium, the 3-methyl group of the diene **9**, lying in the plane of the chromophore at the equilibrium nuclear configuration, makes a $\pi_2 \rightarrow \pi_3^*$ CD contribution of similar magnitude, $\Delta\epsilon$ +0.32 (20 °C), $\Delta\epsilon$ +0.44 (−180 °C) at 282 nm.

In a recent experimental and theoretical study of the optical activity of (+)-(5*R*)-methyl-1,3-cyclohexadiene and its analogues, it is found[2] that, while the axial allylic 5-methyl group makes the major contribution to the $\pi_2 \rightarrow \pi_3^*$ rotational strength, the corresponding equatorial 5-methyl group contributes to a minor degree, comparable to that of a 4-methyl group, or the chromophore torsional helicity, each of the latter contributions amounting to some 14% of that of the axial 5-methyl group, with the opposite sign. A 2-methyl substituent in the 1,3-diene chromophore is estimated to make a contribution to the $\pi_2 \rightarrow \pi_3^*$ rotational strength of the same sign as that of the axial 5-methyl group but only at the 3% level.[2]

The calculations, carried out ab initio with a minimal basis set, excluding the Rydberg orbitals, refer to a 1,3-cyclohexadiene

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system with a torsion angle of 17° between the C_1–C_2 and C_3–C_4 bonds,[2] and the results are not directly transferable to dienes with a zero torsion angle at equilibrium. Thus, the 3-methyl group of the diene **9** makes a larger contribution to the $\pi_2 \rightarrow \pi_3^*$ CD than the 2-methyl group of the diene **7** (Figures 2–5).

In the latter case, and that of the 2-deuterio diene **6**, the bisignate CD gives a vanishing sum over the 300–250-nm range. Each vibronic component in the excited-state C=C stretching progression of the $\pi_2 \rightarrow \pi_3^*$ transition is associated with a bisignate CD couplet, where a further splitting is observed in the negative subcomponent in the gas phase spectrum of **6** or the positive subcomponent in the −180 °C spectrum of **7** (Figures 1 and 5). These observations suggest that the chiral distortion of the diene chromophore in **6** and **7**, allowing a colinear electric and magnetic transition moment, is dynamic, arising from a vibrational mode or modes with inequivalent turning points, due to the mass difference between the groups occupying the 2- and 5-positions in each of these dienes. The out-of-plane bending modes of the groups in the 2-position of the dienes **6** and **7** are expected to be the most effective, although only the higher frequency excited-state C=C stretching modes are identified in the present low-resolution spectra.

The $\pi_2 \rightarrow \pi_3^*$ CD of the 3-methyl diene **9** is monosignate with a rotational strength of $+1.3 \times 10^{-40}$ cgs, a value that is of the expected[2] order (~3%) of the rotational strength due to an axial 5-alkyl group substituted into 1,3-cyclohexadiene[2] (48.2 for the isopropyl group, 55.6 for the *tert*-butyl group, in units of 10^{-40} cgs). However, the rotational strength of **9** is some 7 times larger than that of the 3-deuterio diene **8**, a factor close to the mass ratio of the substituents replacing hydrogen in the parent diene. The relation suggests a common vibronic perturbation of the symmetric diene chromophore in the two cases, **8** and **9**.

The substantial CD absorption of the methyl-substituted dienes **7** and **9** in the shorter wavelength region, 250–180 nm, compared with the corresponding CD of the deuterio analogues **6** and **8**, indicates that electron delocalization encompassing the methyl substituent is significant in the Rydberg excited states of **7** and **9**. The vibronic loss of substituent–diene coplanarity in the deuterio dienes **6** and **8** gives rise to optical activity with a common small magnitude in the N → V_1 and N → R regions of the spectra, suggesting that the V_1 and R excited states are changed to only a minor degree by deuterio substitution, whereas the diffuse 3p Rydberg states in the dienes **7** and **9** include larger electronic contributions from the methyl substituents than the corresponding V_1 states ($\pi_2^{-1}\ \pi_3^*$).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian EM-390, Bruker HX-90, and Bruker WP-200 instruments, and apparent splittings are given. An AEI-MS9 spectrometer operating at an ionization energy of 70 eV was used for the mass spectral measurements. Optical rotation data were determined on a Perkin-Elmer Model 241 polarimeter. Preparative scale VPC separations were performed with Varian Aerograph Model A90-P3 instruments equipped with thermal conductivity detectors. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2-(Trimethylsiloxy)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (10). Freshly distilled nopinone (12.5 g, 0.091 mol), $[\alpha]^{25}_D$ +16.90° (neat), was added to a mixture of chlorotrimethylsilane (19 mL, 0.148 mol) and triethylamine (40 mL, 0.285 mol) in dimethylformamide (40 mL). The solution was heated to reflux under a dryng tube for 18 h, cooled, and poured onto a stirred ice-cold solution of sodium bicarbonate containing crushed ice. The mixture was extracted with pentane (3 × 200 mL) and the combined organic layers were washed with saturated sodium bicarbonate solution, dried, and evaporated to leave a brown liquid. Distillation gave **10** as a colorless liquid, bp 85–88 °C (5 torr), contaminated by nopinone. High-pressure liquid chromatography (Waters Prep 500, elution with petroleum ether–ethyl acetate, 97:3) afforded pure silyl enol ether (15.2 g, 80%): IR (neat, cm^{-1}) 3040, 2940, 2910, 2830, 1645, 1333, 1248, 1215, 1180, 1122, 914, 870, 834; ^{1}H NMR ($CDCl_3$) δ 4.51 (br s, 1 H), 2.6–1.9 (m, 6 H), 1.33 (s, 3 H), 0.96 (s, 3 H), 0.23 (s, 9 H); *m/e* (M^+) calcd 210.1400, obsd 210.1445.

3-Bromo-7,7-dimethylbicyclo[4.1.1]oct-3-en-2-one (11). Trimethylsilyl enol ether **10** (10.37 g, 49.3 mmol) was dissolved in 40 mL of pentane, and potassium *tert*-butoxide (13.80 g, 123 mmol) was added all at once while the solution was stirred at −25 °C. bromoform (8.63 mL, 98.6 mmol) was added slowly in pentane solution (20 mL), and the mixture was allowed to warm to room temperature overnight, diluted with pentane, and poured into ice water. The aqueous layer was extracted with pentane, and the combined organic layers were dried and evaporated to yield a brown oil, which was filtered through Florisil (elution with petroleum ether–ethyl acetate, 95:5). After a small forerun, distillation at 110–115 °C (0.1 mm) and chromatography on a 50 × 4 cm bed of active Florisil (elution with petroleum ether–ethyl acetate, 98:2, changing to 95:5 after 1500 mL) gave 7.0 g (62%) of **11**: IR (neat, cm^{-1}) 2950, 2860, 1670, 1600, 1455, 1405, 1380, 1344, 1215, 1198, 865; ^{1}H NMR ($CDCl_3$) δ 7.01 (t, *J* = 4.5 Hz, 1 H), 2.86 (dd, *J* = 7.5 and 4.5 Hz, 1 H), 2.59 (t, *J* = 3.7 Hz, 2 H), 2.56–1.92 (series of m, 2 H), 1.79 (d, *J* = 7.5 Hz, 2 H), 1.33 (s, 3 H), 0.92 (s, 3 H); *m/e* (M^+) calcd 228.0150, obsd 228.0157.

***endo*-3-Bromo-7,7-dimethylbicyclo[4.1.1]oct-4-en-2-one (12).** After a sample of **11** (63.6 g, 0.303 mol) had been treated as above with potassium *tert*-butoxide (84.8 g, 0.757 mol) and bromoform (53.2 mL, 0.606 mol), the crude product was heated to 40 °C for several hours (0.1 mm) and then filtered through Florisil with pentane. After the mixture was distilled (up to 85 °C, 0.5 mm) to separate the final traces of nopinone, the viscous brown oil remaining in the flask was taken up on Florisil, chromatographed, and distilled as before to yield an oil that darkened. A final chromatography yielded 17 g of nearly colorless oil that partially crystallized on cooling. This solid was separated by filtration and washed with cold hexane: mp 70.5–71.5 °C; IR (KBr, cm^{-1}) 3025, 2970, 2950, 2940, 2865, 1705, 1463, 1389, 1300, 1243, 1162, 860, 817, 784, 720, 599; ^{1}H NMR ($CDCl_3$) δ 6.55 (dd, *J* = 12 and 4 Hz, 1 H), 5.88 (dd, *J* = 12 and 1.5 Hz, 1 H), 5.09 (br d, *J* = 1.5 Hz, 1 H), 2.91–2.40 (m, 3 H), 2.08 (d, *J* = 9 Hz, 1 H), 1.40 (s, 3 H), 1.00 (s, 3 H); *m/e* (M^+) calcd 149.0966, obsd 149.0972; $[\alpha]^{24}_D$ −168°, $[\alpha]^{24}_{436}$ −256° (*c* 2.86, $CHCl_3$).

Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42, H, 5.72. Found: C, 52.69, H, 5.82.

2-Hydroxy-*endo*-3-bromo-7,7-dimethylbicyclo[4.1.1]oct-4-ene (13a). The β,γ-unsaturated α-bromoketone **12** (115 mg, 0.50 mmol) was dissolved in benzene (2 mL) and cooled in an ice bath. Diisobutylaluminum hydride (0.55 mL of a 1 M solution in hexane, 0.55 mmol) was added at a rapid dropwise rate. The reaction mixture turned yellow during the addition, but the color disappeared when the full equivalent was reached. After 2 h at 0 °C, the reaction mixture was quenched by careful addition of 50% aqueous methanol (1 mL). The resulting mixture was partitioned between ether and 3 N sodium hydroxide solution, and the ether layer was washed with water and brine, dried, and evaporated to yield a white crystalline solid (109 mg, 94%): mp 87.5–88 °C (from hexane; IR (KBr, cm^{-1}) 3245, 2940, 1445, 1360, 1265, 1032, 997, 743, 688; ^{1}H NMR ($CDCl_3$) δ 6.0–5.5 (m, 2 H), 5.00 (br s, 1 H), 4.42 (br s, 1 H), 2.6–2.2 (m, 3 H), 1.55 (d, *J* = 9 Hz, 1 H), 1.52 (s, 1 H), 1.33 (s, 3 H), 1.07 (s, 3 H); *m/e* 230 (M^+).

Anal. Calcd for $C_{10}H_{15}BrO$: C, 51.97; H, 6.54. Found: C, 52.18; H, 6.64.

2-Hydroxy-[2-^{2}H]-*endo*-3-bromo-7,7-dimethylbicyclo[4.1.1]oct-4-ene (13b). A sample of **12** (941 mg, 4.11 mmol), dissolved in methanol (40 mL) containing cerous chloride hexahydrate (1.46 g, 4.11 mmol) was treated portionwise with sodium borodeuteride over 5 min at 0 °C. After an additional 10 min, the mixture was poured into 0.2 N sodium hydroxide solution (40 mL) containing ice chunks and extracted with ether (100 mL). The aqueous phase was treated with 3 N sodium hydroxide solution (15 mL), and the combined ether layers were washed with water and brine (100 mL each), dried, and evaporated. The crystalline product was recrystallized from pentane–hexane to yield 533 mg of crystals, mp 84–86 °C. An additional 171 mg was obtained by silica gel chromatography (petroleum ether–ethyl acetate) of the mother liquor: the ^{1}H NMR spectrum (in $CDCl_3$) is essentially identical with that of **13a** except for the absence of the broad singlet at δ 4.42, ≥95% *d* by integration. In addition, the downfield region of the spectrum was simplified compared to **13a**: 5.74 (dd, *J* = 12 and 3.5 Hz, 1 H), 5.62 (d, *J* = 12 Hz, 1 H), 5.00 (t, *J* = 3.5 Hz, 1 H); $[\alpha]^{25}_D$ −248°, $[\alpha]^{25}_{365}$ −1095° (*c* 1.20, EtOH).

The enantiomeric purity of **13b** was determined as follows. The bromohydrin (31.9 mg, 0.137 mmol) was dissolved in dichloromethane (6 mL) containing (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (37.5 mg, 0.164 mmol). After the solution was stored for 5 days in the refrigerator, TLC showed continued presence of the bromohydrin, so an additional two drops of the acid chloride were introduced, and the mixture was allowed to stand at room temperature for 5 more days. The mixture was partitioned between ether and water. The organic layer was washed successively with 1 N hydrochloric acid, saturated sodium bicarbonate solution, and water, dried, and evaporated. Most of the sample was chromatographed on silica gel (petroleum ether–ethyl acetate, 95:5)

to yield 54.7 mg of the ester free of anhydride. ^{19}F NMR ($CDCl_3$, δ relative to α,α,α-trifluorotoluene) 8.83 (major diastereomer, 93.5%), 8.59 (minor diastereomer, 6.5%), or 87% ee; this value was corroborated by integration of the ^1H NMR (in $CDCl_3$) signals at δ 3.56 and 3.48, respectively.

2-Acetoxy-*endo*-3-bromo-7,7-dimethylbicyclo[4.1.1]oct-4-ene (14a). Bromohydrin **13a** (58 mg, 0.25 mmol) was dissolved in dichloromethane (1.5 mL). Pyridine (36 μL, 0.44 mmol) and acetyl chloride (24 μL, 0.33 mmol) were added in succession at 0 °C whereupon a white precipitate formed. The stoppered flask was stored in a freezer overnight, warmed to room temperature, poured onto ice water, and extracted with dichloromethane (2 × 5 mL). The combined organic layers were extracted with ice-cold 1 N hydrochloric acid (20 mL), washed with water and brine, dried, and evaporated to leave a pale yellow oil (54 mg, 94%). A sample was further purified by preparative TLC on silica gel (elution with petroleum ether–ethyl acetate, 92:8): IR (neat, cm^{-1}) 2930, 2860, 1730, 1365, 1225, 1010, 965, 752; ^1H NMR ($CDCl_3$) δ 6.10–5.80 (m, 1 H), 5.67–5.40 (m, 3 H), 4.99 (br s, 1 H), 2.63–2.17 (m, 3 H), 2.03 (s, 3 H), 1.62 (d, J = 9 Hz, 1 H), 1.30 (s, 3 H), 1.05 (s, 3 H); m/e (M^+) calcd 272.0412, obsd 272.0421.

7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene (4). Bromoacetate **14a** (50.7 mg, 0.186 mmol) was dissolved in dimethoxyethane (3 mL) and treated with zinc dust (60.7 mg, 0.928 mmol) at reflux for 2 h and for an additional 0.5 h in the presence of a crystal of zinc chloride. The cooled mixture was decanted into water and extracted with pentane. The pentane layer was washed with water (2×), dried, and concentrated by atmospheric distillation before being filtered through a plug of silica gel with pentane. The resulting solution was concentrated again and purified by preparative VPC (12 ft × 0.25 in. 5% SE-30 on Chromosorb G, 120 °C) to yield 7.8 mg (31%) of a colorless oil having spectral data consistent with that reported:[13] ^1H NMR ($CDCl_3$) δ 6.21–5.74 (m, 4 H), 2.68–2.34 (m, 3 H), 1.28 (s, 3 H), 1.11 (d, J = 7.5 Hz, 1 H), 0.80 (s, 3 H).

(+)-(1*S*)-[2-^{2}H]-7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene (6). The deuterium-substituted bromohydrin **14b** (405 mg, 1.74 mmol) was treated as before with acetyl chloride (163 μL, 2.3 mmol) and pyridine (251 μL, 3.1 mmol) in dichloromethane (10 mL) to yield, after silica gel chromatography (petroleum ether–ethyl acetate, 9:1), 413 mg (87%) of pure acetate as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.94 (d of m, J = 13 Hz, 1 H), 5.52 (d, J = 13 Hz, 1 H), 5.00 (br s, 1 H), 2.63–2.17 (m, 3 H); m/e calcd 273.0475, obsd 273.0485, with d incorporation = 94 ± 3%.

The acetate prepared above was treated with zinc dust (494 mg, 7.55 mmol) in dimethoxyethane (25 mL) at reflux for 2 h; fresh zinc was added, and reflux was continued for 1 h. Workup as before followed by preparative VPC yielded 20 mg of pure **6**: ^1H NMR ($CDCl_3$) δ 6.13–5.85 (m, 3 H), 2.65–2.45 (m, 3 H), 1.29 (s, 3 H), 1.08 (d, J = 9.0 Hz, 1 H), 0.80 (s, 3 H); m/e (M^+) calcd 135.1158, obsd 135.1163; $[\alpha]^{25}_D$ +2.3°, $[\alpha]^{25}_{365}$ +7.7° (c 0.13, $CHCl_3$).

(+)-(1*R*)-2,7,7-Trimethylbicyclo[4.1.1]octa-2,4-diene (7). A mixture of **16** and **17** (92 mg, 0.39 mmol), prepared according to the literature reports,[22] was dissolved in dry ether (5 mL) and treated at 0 °C with n-butyllithium (0.76 mL of a 1.58 M solution in hexane, 1.2 mmol). After the solution was stirred at 0 °C for 3 h, the reaction mixture was quenched with water and partitioned between ether and water. The organic phase was washed with water, dried, and evaporated. Preparative VPC purification (12 ft × 0.25 in. 15% SE-30 on Chromosorb G, 115 °C) gave pure **7**: ^1H NMR ($CDCl_3$) δ 6.03–5.65 (m, 3 H), 2.63–2.23 (m, 3 H), 1.81 (s, 3 H), 1.26 (s, 3 H), 1.17 (d, J = 6.4 Hz, 1 H), 0.77 (s, 3 H); λ_{max} (C_2H_5OH) 305 (ϵ 1530), 294 (3180), 283 (3530); $[\alpha]^{22}_D$ +26.4°, $[\alpha]^{22}_{365}$ +162.6° (c 0.0027, $CHCl_3$); m/e (M^+) calcd 148.1252, obsd 148.1258.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.95.

***exo*-2-Hydroxy-3-bromo-7,7-dimethylbicyclo[4.1.1]oct-3-ene (18).** A solution of **11** (1.15 g, 5.0 mmol) in benzene (20 mL) was treated dropwise at 0 °C with diisobutylaluminum hydride (10.0 mL, 10.0 mmol as a 1 M solution in hexane). The mixture was warmed to room temperature, stirred for 3.25 h, quenched with 50% aqueous methanol, and partitioned between ether and 3 N sodium hydroxide solution. The ether layer was washed with water and brine, dried, and evaporated to yield 1.02 g (88%) of a colorless oil: IR (neat, cm^{-1}) 3440, 2900, 2800, 1640, 1455, 1410, 1380, 1360, 1245, 1040, 1010, 990, 840; ^1H NMR ($CDCl_3$) δ 6.11 (t, J = 4.5 Hz, 1 H), 4.31 (br s, 1 H), 2.5–2.2 (m, 4 H), 2.2–1.5 (m, 2 H), 1.34 (s, 3 H), 1.11 (s, 3 H); m/e 230 (M^+); $[\alpha^{27}]_D$ −26.7°, $[\alpha]^{27}_{365}$ −97.7° (c 0.20, EtOH).

***exo*-2-Hydroxy-[3-^{2}H]-7,7-dimethylbicyclo[4.1.1]oct-3-ene (19).** n-Butyllithium (25 mL of a 1.58 M solution in hexane, 39 mmol) was added slowly to a solution of **18** (3.02 g, 13.13 mmol) in ether (90 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. Deuterium oxide (99.96% d, 1 mL) was added dropwise to the cooled mixture, which was stirred for an additional 0.5 h. The mixture was partitioned between ether and water, and the ether layer was dried and evaporated. Trituration with pentane at 0 °C gave, in two crops, 1.81 g (90%) of white crystals; mp 89–90 °C (from hexane); IR (KBr, cm^{-1}) 3400, 2910, 2890, 2860, 2202, 1650, 1460, 1450, 1440, 1410, 1375, 1355, 1315, 1270, 1035, 965; ^1H NMR ($CDCl_3$) δ 5.59 (br s, 1 H), 4.29 (br s, 1 H), 2.5–1.4 (m, 6 H), 1.30 (s, 3 H), 1.10 (s, 3 H); m/e (M^+) calcd 153.1265, obsd 153.1268; d incorporation = 92%, $[\alpha]^{27}_D$ −67°, $[\alpha]^{27}_{365}$ −226° (c 0.70, EtOH).

[3-^{2}H]-7,7-Dimethylbicyclo[4.1.1]oct-3-en-2-one (20). A solution of **19** (1.0 g, 6.5 mmol) in dry dichloromethane (20 mL) was stirred at room temperature for 0.5 h with activated manganese dioxide (5 g, 57 mmol). The mixture was filtered through a Celite pad, the residue was rinsed thoroughly with the same solvent, and the filtrate was evaporated. There was isolated 0.95 g (97%) of **20** as a colorless oil; ^1H NMR ($CDCl_3$) δ 6.58–6.25 (m, 1 H), 2.80–2.55 (m, 3 H), 2.50–2.22 (m, 2 H), 1.82 (d, J = 9 Hz, 1 H), 1.37 (s, 3 H), 0.98 (s, 3 H).

The tosylhydrazone was obtained in 61% yield as a 1:1 mixture of geometric isomers after medium-pressure liquid chromatography on silica gel (elution with petroleum ether–ethyl acetate, 4:1).

(1*S*)-[3-^{2}H]-7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene (8). To a solution of diisopropylamine (2.5 mL, 18 mmol) in dry tetrahydrofuran (30 mL) under nitrogen was added n-butyllithium (10 mL of 1.8 M solution in hexane, 18 mmol) followed by hexamethylphosphoramide (3.0 mL, 18 mmol). To the resulting deep yellow reaction mixture was added during 5 min via syringe a solution of **21** (900 mg, 2.7 mmol) in dry tetrahydrofuran (12 mL). As the addition proceeded, a deep burgundy-red color developed. The mixture was heated at reflux for 1.5 h before being cooled to 0 °C and quenched with water (2 mL). Following partitioning between water and pentane, the aqueous phase was treated with solid sodium chloride and extracted with pentane (2 × 50 mL). The combined organic layers were washed with brine, dried, and evaporated to leave a yellow oil. This material was taken up in dichloromethane (2 mL) and eluted through a short column of alumina to give 170 mg (45%) of **8** as a colorless oil. VPC purification (12 ft × 0.25 in. 15% SE-30 on Chromosorb G, 105 °C) gave the analytical sample: ^1H NMR ($CDCl_3$) δ 6.17–5.77 (m, 3 H), 2.67–2.33 (m, 3 H), 1.28 (s, 3 H), 1.10 (d, J = 7.5 Hz, 1 H), 0.79 (s, 3 H); m/e (M^+) calcd 135.1158, obsd 135.1164.

3,7,7-Trimethylbicyclo[4.1.1]oct-3-en-2-one (22). n-Butyllithium (220 mL of a 1.37 M solution in hexane, 0.30 mol) was added over a period of 3.5 h to a stirred mixture of **10** (12.0 g, 0.10 mol) and 1,1-dichloroethane (40 g, 0.4 mol) in anhydrous ether (50 mL) at −50 to −40 °C. The stirred mixture was allowed to warm slowly to about 0 °C, poured onto water, and washed twice with water. The organic layer was dried and evaporated to yield 24.8 g of an orange oil, which was separated by high-pressure liquid chromatography on silica gel (Waters Prep 500, elution with petroleum ether–ethyl acetate, 95:5) to yield 2.88 g (18%) of **22**: IR (neat, cm^{-1}) 2950, 2870, 1655, 1450, 1380, 1200, 1030, 842; ^1H NMR ($CDCl_3$) δ 6.40–6.21 (m, 1 H), 2.77 (dd, J = 7.5 and 4.5 Hz, 1 H), 1.85 (br s, 3 H), 1.72 (d, J = 9 Hz, 1 H), 1.30 (s, 3 H), 0.90 (s, 3 H); m/e (M^+) calcd 164.1201, obsd 164.1205; $[\alpha]^{20}_D$ +18.2°, $[\alpha]^{20}_{436}$ +145° (c 1.22, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.51; H, 9.86.

The remaining fractions from the above chromatography were found to contain nopinone (5.3 g, 40%) and a component (12 g, 40%) whose spectral data were consistent with an intact carbene adduct: IR (neat, cm^{-1}) 2920, 2860, 1258, 1248, 1192, 1147, 1037, 885, 866, 835, 748; ^1H NMR (CCl_4) δ 2.4–1.8 (series of m, 6 H), 2.00 (s, 3 H), 1.36 (s, 3 H), 1.18 (s, 3 H), 0.33–0.10 (m, 1 H), 0.23 (s, 9 H); m/e calcd 272.1363, obsd 272.1374.

When the above compound was subjected to reflux in methanol–triethylamine (85:15) for 12 h, the sole identifiable product was found to be **23**. The same product was obtained on thermolysis in xylene at reflux: IR (neat, cm^{-1}) 2920, 1699, 1629, 1250, 1212, 1197; ^1H NMR ($CDCl_3$) δ 6.96 (tq, J = 7 and 5 Hz, 1 H), 2.77–2.43 (m, 4 H), 2.43–2.17 (m, 1 H), 1.80 (dt, J = 7 and 1.5 Hz, 3 H), 1.53–1.3 (m, 1 H), 1.33 (s, 3 H), 0.84 (s, 3 H); m/e (M^+) calcd 164.1201, obsd 164.1205.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.37; H, 9.81.

***exo*-2-Hydroxy-3,7,7-trimethylbicyclo[4.1.1]oct-3-ene (24).** A solution of **22** (2.88 g, 17.5 mmol) in benzene (70 mL) was cooled with an ice bath and treated dropwise with diisobutylaluminum hydride (35 mL of a 1 M solution in hexane, 35 mmol). After 0.5 h, the mixture was allowed to warm to room temperature for 3.5 h. The reaction mixture was quenched by slow addition of methanol–water (1:1, 20 mL) with cooling and partitioned between ether and 3 N sodium hydroxide solution. The organic layer was washed successively with water and brine, dried, and evaporated to yield 2.80 g (96%) of a colorless oil free of

ketone. This was further purified by high-pressure liquid chromatography on silica gel (Waters Prep 500, elution with petroleum ether–ethyl acetate, 95:5): IR (neat, cm^{-1}) 3620, 3440, 2955, 2905, 2875, 1642, 1455, 1425, 1387, 1319, 1040, 922; ^1H NMR ($CDCl_3$) δ 5.37 (br s, 1 H), 4.06 (br s, 1 H), 2.48–2.17 (m, 4 H), 2.17–1.9 (m, 1 H), 1.88 (s, 3 H), 1.48 (s, 1 H), 1.3–1.14 (m, 1 H), 1.27 (s, 3 H), 1.08 (s, 3 H); *m/e* (M^+) calcd 166.1358, obsd 166.1352; $[\alpha]^{27}_D$ −30.9, $[\alpha]^{27}_{365}$ −3.0° (*c* 1.45, EtOH).

The enantiomeric purity of **24** was determined as follows. The alcohol (23.3 mg, 0.14 mmol) was treated in the same manner as **19**. After chromatography of most of the sample, 45 mg of ester was obtained. ^{19}F NMR ($CDCl_3$, δ relative to α,α,α-trifluorotoluene) 8.55 (major diastereomer, 94.7%), 7.83 (minor diastereomer, 5.3%), or 89% ee; this value was corroborated by integration of ^1H NMR (in $CDCl_3$) signals of δ 3.60 and 3.48, respectively.

(+)-(1*S*)-3,7,7-Trimethylbicyclo[4.1.1]octa-2,4-diene (9). A. Dehydration of 24. A solution of 24 (48 mg, 0.30 mmol) in triethylamine (4 mL) and dichloromethane (2 mL) was treated at −20 °C with methanesulfonyl chloride (163 μL, 2.1 mmol). The mixture was stirred for 0.5 h and warmed to room temperature for an additional 0.5 h. Two such runs were quenched with water, combined, and diluted with pentane. The organic layer was washed with 10% potassium bisulfate solution and water, dried, concentrated, and filtered through Florisil with pentane. Preparative VPC (12 ft × 0.25 in. 15% SE-30 on Chromosorb G, 145 °C) gave 4.3 mg of **9**: ^1H NMR ($CDCl_3$) δ 6.09–5.95 (m, 1 H), 5.84–5.71 (m, 2 H), 2.59–2.33 (m, 3 H), 1.85 (d, J = 1.5 Hz, 3 H), 1.25 (s, 3 H), 1.17–1.05 (m, 1 H), 0.78 (s, 3 H); λ_{max} (C_2H_5OH) 305 (ϵ 1010), 294 (2220), 283 (2490); $[\alpha]^{25}_D$ +0.7, $[\alpha]^{25}_{365}$ +78.5° (*c* 0.145, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.12; H, 10.84.

B. Shapiro Reaction on 22. A solution of **22** (2.0 g, 12.2 mmol) and (*p*-toluenesulfonyl)hydrazine (2.72 g, 14.6 mmol) in methanol (15 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by high-pressure liquid chromatography (elution with petroleum ether–ethyl acetate, 85:15) to give the tosylhydrazone (2.62 g, 65%) as a colorless crystalline solid, mp 162–165 °C dec (from petroleum ether–ethyl acetate).

A 1.5-g (4.5 mmol) sample of the tosylhydrazone was added to a solution of diisopropylamine (40 mL, 29 mmol), *n*-butyllithium (18 mL of a 1.5 M solution, 27 mmol), and hexamethylphosphoramide (4.8 mL, 29 mmol) in the manner described above. Following chromatography on alumina, **9** was obtained as a colorless oil (350 mg, 52%), identical in all respects with the hydrocarbon obtained in A.

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Registry No. (1*S*)-**4**, 62235-10-3; (1*S*)-**6**, 86689-39-6; (1*R*)-**7**, 86689-40-9; (1*S*)-**8**, 86689-41-0; (1*S*)-**9**, 86689-42-1; (1*R*)-**10**, 72453-33-9; (1*R*)-**11**, 86689-43-2; (1*R*)-**12**, 86689-44-3; **13a**, 86689-45-4; **13b**, 86689-46-5; (1*R*)-**13b** (−)-α-methoxy-α-(trifluoromethyl)phenylacetate (isomer 1), 86689-47-6; (1*R*)-**13b** (−)-α-methoxy-α-(trifluoromethyl)-phenylacetate (isomer 2), 86709-31-1; **14a**, 86689-48-7; **14b**, 86689-49-8; (1*R*)-**16**, 34153-03-2; (1*R*)-**17**, 86709-32-2; (1*R*)-**18**, 86689-50-1; (1*R*)-**19**, 86689-51-2; (1*R*)-**20**, 86689-52-3; (1*R*)-(*E*)-**21**, 86689-53-4; (1*R*)-(*Z*)-**21**, 86709-33-3; (1*R*)-**22**, 86689-54-5; (1*R*)-**22** tosylhydrazone, 86695-74-1; (1*R*)-(*E*)-**23**, 72453-37-3; (1*R*)-**24**, 86689-55-6; (1*R*)-**24** (−)-α-methoxy-α-(trifluoromethyl)phenylacetate (isomer 1), 86689-56-7; (1*R*)-**24** (−)-α-methoxy-α-(trifluoromethyl)phenylate (isomer 2), 86709-34-4; (+)-nopinone, 38651-65-9; (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 39637-99-5.

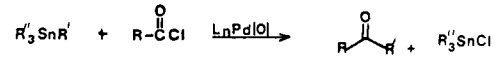
Mechanisms of the Palladium-Catalyzed Couplings of Acid Chlorides with Organotin Reagents

Jeff W. Labadie and J. K. Stille*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received February 22, 1983*

Abstract: In the coupling reaction of benzoyl chloride with phenyltributyltin catalyzed by the introduction of benzylchlorobis(triphenylphosphine)palladium(II) (**1**), the disappearance of **1** was observed in the ^{31}P spectrum of the reaction mixture with the appearance of benzoylchlorobis(triphenylphosphine)palladium(II) (**3**); benzophenone was obtained as a product of the reaction. The reaction of **3** with phenyltributyltin also yields benzophenone and is retarded by added triphenylphosphine. The results are consistent with a catalytic cycle involving sequential fast oxidative addition of benzoyl chloride to a palladium(0) complex (generated from **1**) to give **3**, slow transmetalation of **3** with the tin reagent, and fast reductive elimination to regenerate the palladium(0) complex. The rates of the transmetalation reaction of unsymmetrical organotrimethyltin or organotributyltin ($R'SnR_3$) with **3** in the catalytic reaction followed the order R′ = PhC≡C > PrC≡C > PhCH=CH, CH_2=CH > Ph > $PhCH_2$ > CH_3OCH_2 > CH_3 > Bu. The transfer of benzyl groups, R′, from tin to **3** is accelerated to some extent by +σ substituents in polar solvents, showing a slightly positive ρ, 1.2. Vinyltin reagents appear to undergo transmetalation with **3** (catalytic reaction) predominately with retention of geometry at the double bond. Inversion of configuration at carbon takes place at an sp^3 carbon (R′) bound to tin when the transmetalation reaction of **3** is carried out in a polar solvent. These results are consistent with a transmetalation reaction in which electrophilic cleavage of the carbon–tin bond takes place, with palladium(II) (**3**) acting as the electrophile.

The palladium-catalyzed coupling reaction of acid chlorides with organotin reagents has been demonstrated to be an efficient reaction that gives ketones in high yields.[1,2] The reaction is quite general with respect to both coupling partners and can be carried out in a number of solvents, including HMPA, chloroform, dichloroethane, and THF. The ketone product is formed rapidly under mild, neutral reaction conditions, and catalytic turnovers of 1000 have been achieved. There is no further addition to the product ketone, and a wide variety of functional groups can be tolerated on the acid chloride, including nitro, nitrile, haloaryl, methoxy, ester, and even aldehyde.[1]



The tetraorganotin reagents transfer the first group rapidly, but the second leaves about 100 times slower from R_3SnCl. More recently, this reaction has been carried out with acetylenic tin

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