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CHIRAL ACETYLENES AS SYNTHETIC INTERMEDIATES—II[a]

OPTICALLY ACTIVE 1,4-DIALKYLBUTA-1,3-DIENES: SYNTHESIS AND CONFORMATIONAL STUDIES

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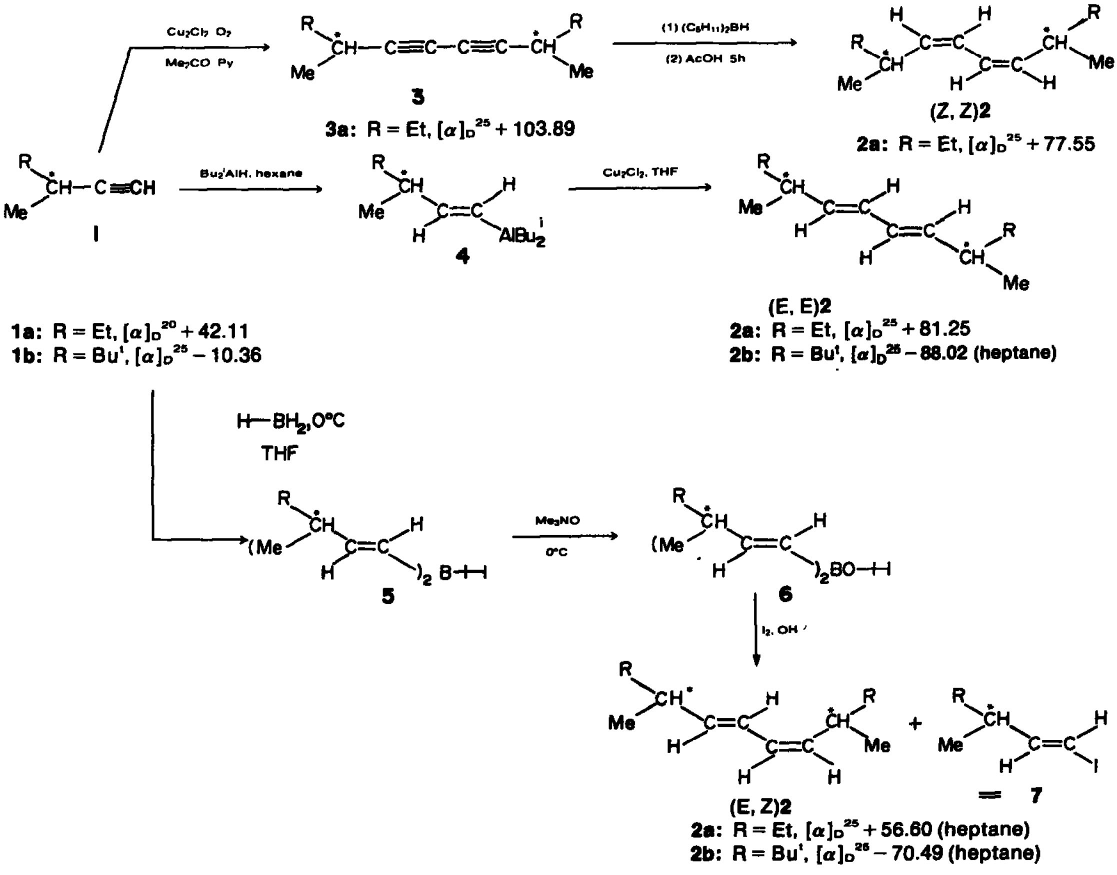
Abstract—The synthesis and the physical properties of some optically active 1,4-dialkylbuta-1,3-dienes are reported. The synthetic processes employed were essentially stereospecific. NMR, UV and CD spectra of these compounds provide information on the main conformation of the conjugated diene system, which was shown to be *s-trans* planar.

While the synthesis[1–11] and study of the physical properties of 1,3-dienes are widely reported, to date only a few optically active alkylbutadienes have been described.[12–15] Recently the synthesis of (E)(3S,7S) - 3,7 - dimethyl - 4 - methylenenon - 5 - ene from (S) - 3 - methylpent - 1 - yne has been reported,[16] and, in this context, it is interesting to note the use of chiral acetylenic substrates for the stereoselective synthesis of 1,4 - dialkylbuta - 1,3 - dienes. The availability of such compounds should permit the investigation of the chirooptical and conformational properties of aliphatic non-rigid chiral dienes.

We report here the synthesis and some conformational studies on a series of optically active 1,4 - dialkylbuta - 1,3 - dienes **2**, having two chiral carbon atoms. We also evaluated the stereospecificity of some synthetic methods reported in literature.[1,5,8]



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[a] For Part I see Ref. 21.

Synthesis of the dienes

(Z,Z)(3S,8S) - 3,8 - Dimethyldeca - 4,6 - diene **2a** was obtained (79% yield) by reduction of the corresponding diyne **3** with dicyclohexylborane in THF, followed by protonolysis by acetic acid[1] (Scheme). Compound **3** was prepared by Glaser's method from (S) - 3 - methylpent - 1 - yne **1a**[17] (78% yield). (Z,Z) **2a** was recovered by distillation from the reaction mixture and then purified by preparative GLC: in fact, the GLC analysis of crude **2a** has shown the presence (9%) of the corresponding enyne system.[1]

The preparation of (E,E)**2** was performed by treating the alkenyldiisobutylalane **4** with cuprous chloride in THF[8] (Scheme). **4** was obtained by addition of diisobutylaluminium hydride to a solution of **1** in hexane. The conversion of **1** into **4** was shown to be incomplete: indeed the GLC analysis of a sample of the reaction mixtures revealed the presence of the alkynyldiisobutylalane derived from **1a**[17] and (R) - 3,4,4 - trimethylpent - 1 - yne **1b**[18] (10% and 20% respectively). The subsequent treatment of **4** with cuprous chloride[8] gave (E,E)**2a** and (E,E)**2b** in 75% and 57% yields respectively.

The synthesis of (E,Z)**2** was carried out via hydroboration of **1** with thexylborane, followed by alkaline iodination[5] (Scheme). Thus, a sample of **1** was converted to **5** and subsequent treatment with trimethylamine *N*-oxide gave the dialkenylborinate **6**. Then **6** was iodinate in alkaline solution and a mixture of (E,Z)**2** and (E) - 1 - iodoalk - 1 - ene **7** was recovered. The yields of the reaction were not excellent, owing to the competitive iodolysis of the alkenyl-boron bond to compound **7**. The migration of the alkenyl groups seems to depend on the bulkiness of the substituents in the α-position with respect to the triple bond in **1**: in fact the yields decrease drastically from (E,Z)**2a** (76%) to (E,Z)**2b** (30%).

It is to be observed that, whereas (E,Z)**2b** was recovered from the reaction mixture by distillative work-up, (E,Z)**2a** was obtained by preparative GLC, as the distillation of the crude compound caused appreciable isomerisation to (E,E)**2a**.[19]

Determination of the optical purity of the dienes

The optical purity of the dienes **2** prepared could be estimated by catalytic hydrogenation to paraffins. However, recent investigations have shown that the hydrogenation of chiral olefins in the presence of Raney-Ni occurs with partial racemisation,[20] moreover the maximum rotatory power of the paraffins is not known with any confidence. For this reason we preferred to use other methods for stereospecifically converting **2** into substrates of known optical purity. Therefore the relationship between the optical purity and the rotatory power of **2** was evaluated by conversion into the corresponding ozonide, followed by reduction with LAH[21] to (S) - 2 - methylbutan - 1 - ol **8a**[22] and (R) - 2,3,3 - trimethylbutan - 1 - ol **8b**[18] (Table 1). The data obtained indicate that the sequences adopted for the synthesis of **2** occurred with high stereospecificity and did not involve the carbon atom in the α-position with respect to the triple bond.

Spectroscopical data and conformational studies

The dienes **2** were characterised by their IR and NMR spectra. The IR spectrum of (Z,Z)**2a** is consistent with the proposed structure, it has three absorptions (stretching vibrations of the double bond) in the 1760–1600 cm^{-1} region and a sharp band (bending-out-of-plane vibration) at 738 cm^{-1}, consistent with the literature[23,24] (Table 2). The IR spectra of (E,E)**2** show the bending-out-of-plane frequencies of conjugated (E) double bonds at 985 cm^{-1},[24] while the IR spectra of (E,Z)**2** reveal two characteristic absorptions at 980 and 947 cm^{-1},[24] and two bands of medium intensity in the 750–720 cm^{-1} region (Table 2). The spectrum of **2a** shows absorptions at 770 cm^{-1}, attributable to the rocking vibrations of the methylene groups, while those of **2b** reveal two bands at 1238 and 1220 cm^{-1}, characteristic of the skeletal vibrations of the 1,2,2-trimethylpropylic group[23] (Table 2).

The NMR spectra of compounds **2** are very complex; initial assignments were made through spin decoupling experiments and by comparison of the spectra with those reported for dienes of similar structures.[12–14,25–27] In particular the resonances of the diene protons were computed with an IBM 370/158 computer using the iterative program LEQUOR 3.[28] Table 3 reports the chemical shifts of the diene protons, together with the relative coupling constants. The diene protons of (Z,Z)**2a** and (E,E)**2** give rise to spectra of the AA'BB' type, while the (E,Z) isomers show spectra of the ABCD type. According to the literature,[26,27] the downfield signals are attributable, in all cases, to the protons at positions 2 and 3. The values of the ^3J_c ($\sim$10 Hz) and ^3J_t constants ($\sim$15 Hz), which are of a diagnostic use in establishing the configuration of the double bonds, confirm the structure of the dienes **2** prepared.

It is known that the most stable conformer of buta-1,3-diene derivatives, not substituted in the 1- and 3-positions, is the planar *s-trans* one,[29] thus a planar *s-trans* form is to be expected also for compounds **2**. In the case of (E,E) and (Z,Z)**2** the planar conformation has an inversion centre and should obey the mutual exclusion rule, implying a limited number of frequencies in the IR

Table 1. Optical activity-optical purity of the dienes 2

Alkyne 1	$[\alpha]_D^{20}$(neat)	Optical purity %	Diene 2	$[\alpha]_D^{25}$	$\mathrm{R(Me)\overset{*}{C}H{-}CH_2OH}$[a] 8	$[\alpha]_D^{25}$(neat)	Optical purity %
1a	+42.11	90.6[b]	(Z,Z)**2a**	+77.55	8a: R = Et	−5.25	90.2[c]
	+41.81	90.0[b]	(E,E)**2a**	+80.67		−5.30	91.0[c]
	+41.28	88.8[b]	(E,Z)**2a**	+55.48 (heptane)		−5.15	88.5[c]
1b	−10.36[d]	82.3[e]	(E,E)**2b**	−88.02 (heptane)	8b: R = Bu^t	−34.30 (ethanol)	82.8[e]

[a] Recovered by reductive ozonolysis of 2. [b] L. Lardicci, C. Botteghi and E. Benedetti, *J. Org. Chem.* **31**, 1534 (1966). [c] R. Rossi, P. Diversi and G. Ingrosso, *Gazz. Chim. Ital.* **98**, 1391 (1968). [d] Determined at 25°C. [e] A. M. Caporusso, G. Giacomelli and L. Lardicci, *Atti. Soc. Toscana Sci. Nat., Mem.* **A80**, 40 (1973).

Table 2. IR absorptions of the dienes 2

	Frequencies (cm^{-1})					
	$\nu_{C=C}$	ν_{C-H}	δ_{Me}	δ_s CH$_2$ δ_{as} Me	ρ_{CH_2}	Skeletal vibrations
(Z,Z)**2a**	1600, 1690, 1750(w)	738(s)	1370, 1380(s)	1455–1465(s)	770(m)	
(E,E)**2a**		985(s)	1370, 1380(s)	1455, 1465(s)	773(m)	
(E,E)**2b**		985(s)	1375, 1385(s)	1455–1475(s)		1220–1238(m)
(E,Z)**2a**		980, 947(s), 747(m)	1370, 1380(s)	1455–1460(s)	770(m)	
(E,Z)**2b**		980, 948(s), 725, 770(m)	1365–1375	1460–1470(s)		1220–1238(m)

spectra.[29] It is interesting to note that ^3J_s values for **2** approach the theoretical value for a planar *s-trans* conformation[31] and the experimental value measured for butadiene (10.4 Hz), which has been reported to be mainly (97%) planar *s-trans*.[32] Even the long-range coupling constants are consistent with **2** having the planar *s-trans* conformation, at least at room temperature.

In addition, $^3J_{vic}$ coupling constants provide some information about the more stable conformations of the bond between the diene carbon atom and the α-chiral carbon atom.[33] These coupling constants are higher in (Z,Z)**2** than in (E,E)**2**; accordingly, these constants are different for (E,Z)**2**. The $^3J_{vic}$ coupling constants related to the (Z) double bonds are *ca.* 10 Hz, whereas those relating to the (E) double bonds decrease to 7–8 Hz, indicating that the prevailing conformers are those having the proton bound to the α-chiral carbon atom *anti* to the (Z) bond and *gauche* to the (E) bond.

UV and CD spectra

The UV spectra of conjugated dienes have been widely studied,[34–37] and some empirical rules relating wavelength of absorption maxima to substitution of the diene chromophore have been derived.[34,37] An investigation of the UV absorption properties of **2**, in heptane at 25°C, gave the data reported in Table 4 and Figs. 1 and 2. In all the cases the UV spectra are characterised, in the 260–190 nm region, by a relatively intense band, centered around 235–230 nm, and assigned to the $\pi-\pi^*$ transition.[35] A comparison of the UV spectra of **2** shows a bathochromic shift of the absorption maxima changing the configuration of **2** from (E,E) to (Z,Z). This red shift may be rationalised by considering that both the alkyl substituents in (Z,Z)**2** can interact with the central single bond of the diene chromophore, in (E,Z)**2** we have only one of these interactions, whereas no interaction is possible in (E,E)**2**.[34]

All the dienes examined show, in addition to the

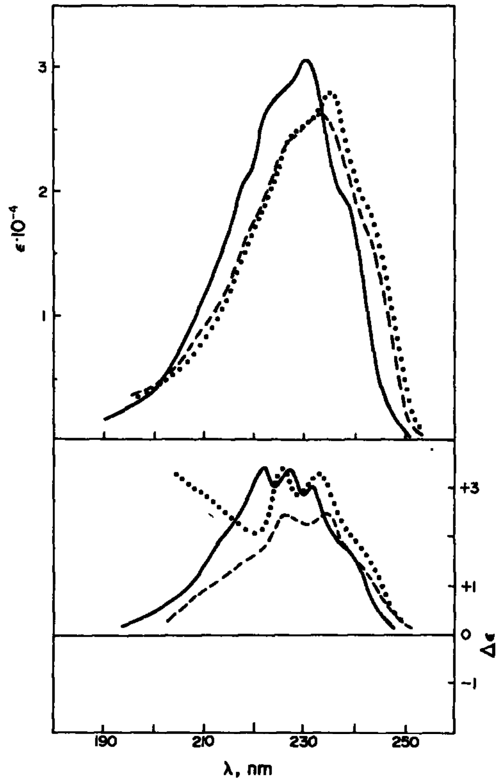


Fig. 1. Absorption spectra (upper curves) and CD spectra (lower curves) of (Z,Z)**2a** (······), (E,Z)**2a** (———), and (E,E)**2a** (——) in heptane at 25°C.

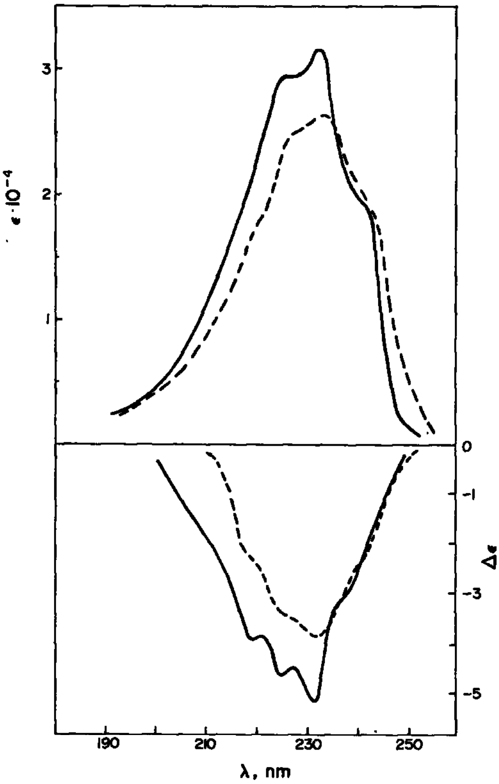


Fig. 2. Absorption spectra (upper curves) and CD spectra (lower curves) of (E,Z)**2b** (------) and (E,E)**2b** (——) in heptane at 25°C.

Table 3. NMR data ($CDCl_3$) of the dienes **2** (100 MHz)

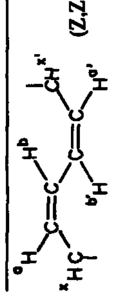
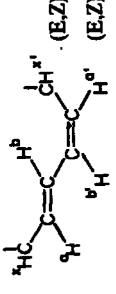
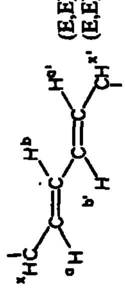
		Chemical shifts (δ) (ppm)						Coupling constants (Hz)									
		H^a	H^b	$H^{a'}$	$H^{b'}$	H^x	$H^{x'}$	^3J_c	^3J_t	^3J_s	^4J_c	^4J_t	$^5J_{tt}$	$^5J_{cc}$	$^5J_{tc}$	$^3J_{vic}$
	(Z,Z)**2a**	5.06	6.12	5.06	6.12	2.48	2.48	10.4	—	11.9	—	−0.3	2.3	—	—	10.3
	(E,Z)**2a**	5.51	6.27	5.05	5.90	2.10	2.50	10.5	14.2	10.5	−0.7	−0.5	—	—	0.6	7.5(J_{ax}) 10.5($J_{a'x'}$)
	(E,Z)**2b**	5.51	6.22	5.18	5.84	1.85	2.40									
	(E,E)**2a**	5.56	5.93	5.56	5.93	2.00	2.00	—	14.9	10.7	−1.1	—	—	0.2	—	7.9
	(E,E)**2b**	5.55	5.90	5.55	5.90	1.95	1.95									

Table 4. UV and CD spectra of the dienes **2** in heptane at 25°C

Diene	UV λ(nm)	UV ε	CD λ(nm)	CD Δε
(Z,Z)**2a**[a]	241 (sh)	19,700	240	+1.9
	235	28,000	233	+3.28
	229 (sh)	24,900	226	+3.3
	220 (sh)	16,800	210 (sh)	+2.8
	212 (sh)	9,800		
(E,Z)**2a**[b]	240 (sh)	18,400	240 (sh)	+1.5
	233	26,200	235	+2.47
	228 (sh)	24,100	226	+2.41
	220 (sh)	18,000	220 (sh)	+1.6
	211 (sh)	9,400	212 (sh)	+1.0
(E,E)**2a**[a]	238 (sh)	19,400	238 (sh)	+1.7
	231	30,500	232	+3.01
	225 (sh)	28,000	227	+3.41
	220 (sh)	22,800	222	+3.41
	210 (sh)	11,700	213 (sh)	+2.0
(E,Z)**2b**[c]	243 (sh)	18,800	241 (sh)	−2.4
	234	26,500	232	−3.85
	228 (sh)	25,200	226 (sh)	−3.5
	220 (sh)	17,300	220 (sh)	−2.4
	210 (sh)	8,700	215 (sh)	−1.1
(E,E)**2b**[c]	240 (sh)	19,700	238 (sh)	−3.2
	233	31,700	232	−5.30
	227	29,500	225	−4.74
	220 (sh)	22,100	220	−4.01
	210 (sh)	11,600	215 (sh)	−1.2

[a]Optical purity 90%. [b]Optical purity 87%. [c]Optical purity 82%.

absorption maxima a series of shoulders at shorter and longer wavelengths. The vibrational spacing of the fine structure observed, which has been generally attributed to vibrational sub-levels,[34] is *ca.* 1100–1450 cm^{-1}, fitting very well the vibrational frequencies of the IR spectra (Table 2).

The UV absorption maxima of the compounds **2** (Table 4) further confirm the prevailing planar *s-trans* conformation. Indeed **2** exhibit high extinction coefficients ($\epsilon \simeq 26{,}000$–$32{,}000$), consistent with dienes which are planar *s-trans*.[34]

The CD spectra of **2**, registered in the 260–190 nm range, show the presence of a band of relatively high intensity, centered approximately at the same wavelength as the UV absorption maximum (Table 4, Figs. 1 and 2). The values of $\Delta\epsilon_{max}$ observed are one order of magnitude greater than those of a diene of similar structure, such as (E)(S) - 5 - methylhepta - 1,3 - diene,[13] and comparable with those of di(4 - methylcyclohexylidene)-ethane, a more rigid diene, which is mainly in a planar conformation.[15] In addition the $\Delta\epsilon_{max}$ values of **2b** are greater than those of **2a** and the difference may be explained on the basis of the higher conformational homogeneity of **2b**. However it is worth noting that the aliphatic chiral dienes prepared show relatively high values of $\Delta\epsilon_{max}$, which put the allied chromophore between the inherently dissymmetric (skewed) and symmetric (asymmetrically substituted) diene chromophore.[15]

Even if the dienes **2** are essentially in a planar conformation, as indicated by IR, NMR and UV measurements, the CD data, collected so far, do not permit us to explain the nature of optical activity in dienes **2** and the slight inherent dissymmetry of the chromophore, twisting of the individual double bonds and the contribution of the chiral centres in the substituents, could be invoked to explain the sign† and intensity of their CD bands.[38]

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer 225 spectrometer as liquid films. NMR spectra were determined in $CDCl_3$ soln on a Jeol JNM-PS-100 (100 MHz) spectrometer and interpreted by using an IBM 370/158 computer: chemical shifts are given in ppm from TMS as the internal standard. Splitting patterns are designed as s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet. UV spectra were measured in heptane at 25°C with a Cary 14 recording spectrophotometer. Mass spectra were taken at 70 eV on a Varian Mat CH7 mass spectrometer; only the main ions are listed. Optical rotations were measured on a Perkin–Elmer 142 automatic spectropolarimeter: unless otherwise specified, rotations refer to pure liquid. CD spectra were recorded on a Jobin-Yvon III Dichrograph in heptane at 25°C. GLC was carried out with a Perkin–Elmer F30A gas chromatograph (flame ionization detectors) equipped with columns (2 m × 0.29 cm i.d.) packed with 5% silicone SE 301 on 80/100 chromosorb A or with 12.5% Apiezon M on 80/100 chromosorb W(NAW) and a Perkin–Elmer F21 preparative gas chromatograph, equipped with 3 m × 0.8 cm column packed with 20% Apiezon M on 45/60 chromosorb A. All air-sensitive reactions were carried out under N_2. Solvents for reactions were purified if necessary before use by distillation from suitable drying agents. Organic extracts were always dried over anhydrous Na_2SO_4. Anhydrous Cu_2Cl_2 was used after accurate purification.[39] Dicyclohexylborane and thexylborane were prepared by adding at −5°C a 1.3 M THF solution of borane to THF solution of cyclohexene and 2 - methyl - 2 - butene respectively.[1,5] Diisobutylaluminium hydride was obtained by heating triisobutylaluminium at 110°C (15 mmHg) for 16 h. (S) - 3 - Methylpent - 1 - yne **1a**, $[\alpha]_D^{20} + 42.11$ and (R) - 3,4,4 - trimethylpent - 1 - yne **1b**, $[\alpha]_D^{25} - 10.36$ were obtained through reported sequences from the corresponding α-olefins.[18,40]

(Z,Z)(3S,8S) - 3,8 - *Dimethyldeca* - 4,6 - *diene* **2a**. A steady stream of oxygen was passed into a well-stirred mixture of 0.05 mol of Cu_2Cl_2, 25 ml of pyridine, 50 ml of anhydrous acetone and 8.2 g (0.10 mol) of **1a**, over a period of 3 h, at 20–40°C. The mixture was then acidified with 30 ml of 6 N HCl. After work-up[1] 6.4 g (78% yield) of (3S,8S) - 3,8 - dimethyldeca - 4,6 - diyne **3a** was obtained, b.p. 106° (15 mmHg), n_D^{25} 1,4738, d_4^{25} 0.8102, $[\alpha]_D^{25} + 103.9$; IR: 2250 cm^{-1}; MS *m/e* (%) 162 (84, M^+), 147 (31), 133 (29), 119 (49), 105 (100), 91 (94), 77 (55), 55 (49), 41 (53).

To 0.07 mol of dicyclohexylborane in THF was added at −5°C a solution of **3a** (5.8 g, 0.035 mol) in 20 ml of THF.[1] The reaction mixture was allowed to come to room temp., then maintained at this temp. for 5 h. The red solution was diluted with 16 ml of glacial acetic acid, then heated at 60°C for 5 h. Oxidation of the resulting dicyclohexylborinate was achieved by adding 56 ml of 6 N NaOH followed by dropwise addition of 17 ml of 36% H_2O_2 at a rate to maintain the reaction mixture at 30–35°C. After 30 min and usual working up,[1] distillation gave 3.8 g (69% yield) of (Z,Z)(3S,8S) - 3,8 - dimethyldeca - 4,6 - diene **2a**. Further GLC purification yielded pure (Z,Z) **2a**, b.p. 62° (4.5 mmHg), n_D^{25} 1.4595, d_4^{25} 0.7690, $[\alpha]_D^{25} + 77.55$. NMR: 0.83 (6 H, t), 0.92 (6 H, d), 1.28 (4 H, m), 2.48 (2 H, m), 5.06 (2 H, t), 6.12 (2 H, dd) p.p.m. MS *m/e* (%) 166 (28, M^+), 137 (41), 109 (45), 96 (39), 95 (61), 81 (100), 67 (28), 57 (17), 55 (28), 53 (14), 43 (11), 41 (39), 39 (14), 29 (22), 27 (11).

(E,E)(3S,8S) - 3,8 - *Dimethyldeca* - 4,6 - *diene* **2a**. Diisobutylaluminium hydride (0.075 mol) was added to a solution of 0.075 mol of **1a**, $[\alpha]_D^{20} + 41.81$, in 30 ml of hexane while maintaining the temp. during addition at 25–30°C.[8] The solution was stirred at room temp. for 30 min, then heated at 50°C for 4 h. After cooling the reaction mixture to room temp., the hexane was removed under reduced pressure and 65 ml of dry THF was added at 0°C. Dry Cu_2Cl_2 (0.05 mol) was added over a period of 10 min at 25–35°C.[8] The resultant dark reaction mixture was kept for 50 min at room temp. before being poured slowly into a 5% H_2SO_4 solution. The organic phase was separated and yielded 75% of (E,E)(3S,8S) - 3,8 - dimethyldeca - 4,6 - diene **2a**. Purification by GLC gave pure (E,E)**2a**, b.p. 92° (17 mmHg), n_D^{25} 1.4627, d_4^{25} 0.7699, $[\alpha]_D^{25} + 80.67$. NMR: 0.81 (6 H, t), 0.93 (6 H, d), 1.28 (4 H, m), 2.00 (2 H, m), 5.42 (2 H, m), 5.93 (2 H, m) p.p.m. MS *m/e* (%) 166 (20, M^+), 137 (41), 109 (45), 96 (34), 95 (54), 81 (100), 67 (34), 57 (37), 55 (42), 53 (16), 43 (26), 41 (52), 39 (16), 29 (29), 27 (16).

(E,E)(3S,8S) - 2,2,3,8,9,9 - *Hexamethyldeca* - 4,6 - *diene* **2b**. The compound was prepared (57% yield) according to the above procedure from **1b**, $[\alpha]_D^{25} - 10.36$. GLC purification yielded pure (E,E) **2b** having m.p. 37°, b.p. 78° (0.5 mmHg), $[\alpha]_D^{25} - 88.02$ (heptane). NMR: 0.83 (18 H, s), 0.93 (6 H, d), 1.95 (2 H, m), 5.55 (2 H, m), 5.90 (2 H, m) p.p.m. MS *m/e* (%) 222 (5, M^+), 165 (9), 123 (6), 109 (22), 95 (7), 81 (64), 57 (100), 41 (22), 29 (15).

(E,Z)(3S,8S) - 3,8 - *Dimethyldeca* - 4,6 - *diene* **2a**. A solution of 0.067 mol of thexylborane in 70 ml of THF was added at 0°C to a solution of 0.134 mol of **1a**, $[\alpha]_D^{20} + 40.26$, in 35 ml of THF.[5] The solution was then stirred for an additional hour at 0–5°C. To the vinylborane solution obtained was added 5.1 g (0.067 mol) of solid trimetilamine *N*-oxide, the reaction mixture was stirred for an additional 1 h and then treated at 0–5°C with 67 ml of 3 N NaOH followed by the dropwise addition of a solution of I_2 (17.0 g, 0.067 mol) in THF (35 ml). Any excess iodine was then decomposed by adding a small amount of aqueous $Na_2S_2O_3$. The diene product was extracted into pentane.‡ Preparative GLC yielded (76%) pure (E,Z)(3S,8S) - 3,8 - dimethyldeca - 4,6 - diene **2a**, b.p. 39° (0.3 mmHg), $[\alpha]_D^{25} + 54.14$ (heptane). NMR: 1.00 (12 H, m), 1.38 (4 H, m), 2.10 (1 H, m), 2.50 (1 H, m), 5.05 (1 H, m), 5.51 (1 H, m), 5.90 (1 H, m), 6.27 (1 H, m) p.p.m. MS *m/e* (%) 166 (12, M^+), 137 (26), 109 (37), 96 (35), 95 (48), 81 (100), 67 (38), 57 (68), 55 (65), 53 (15), 43 (53), 41 (71), 39 (26), 29 (43), 27 (32).

(E,Z)(3S,8S) - 2,2,3,8,9,9 - *Hexamethyldeca* - 4,6 - *diene* **2b**. The compound (E,Z)**2b** was prepared (34%) accordingly.‡ Pure (E,Z)**2b** exhibited m.p. 37°, b.p. 71° (0.04 mmHg), $[\alpha]_D^{25} - 70.49$ (heptane). NMR: 0.93 (18 H, s), 1.07 (6 H, d), 1.85 (1 H, m), 2.40 (1 H, m), 5.18 (1 H, m), 5.51 (1 H, m), 5.84 (1 H, m), 6.22 (1 H, m) p.p.m. MS *m/e* (%) 222 (9, M^+), 165 (13), 124 (9), 109 (22), 95 (10), 81 (48), 57 (100), 41 (17), 29 (10).

Ozonolysis of dienes **2**. This procedure is representative for all cases. Compound (E,E)**2a** (1.5 g, 9.2 mmol, $[\alpha]_D^{25} + 80.67$) in 30 ml of pentane was treated at −78°C with the theoretical amount of ozone. The solvent was removed at reduced pressure and the reaction mixture, diluted with diethyl ether, was decomposed with $LiAlH_4$ (1.74 g) in ether solution (50 ml). (S) - 2 - Methylbutan - 1 - ol, n_D^{25} 1.4088, $[\alpha]_D^{25} - 5.30$,[22] was recovered in 59% yield by preparative GLC.

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†It is to observe that dienes **2b** show negative CD bands, whereas dienes **2a** exhibit positive Cotton effects, although their absolute configurations are the same according to the IUPAC rules. It is however to be considered that for the individual series of **2**, the same conventional configuration corresponds to an opposite chirality of the asymmetric carbon atom. Thus the sign of the Cotton effects is in agreement with the actual chirality of the dienes **2**.

‡From the reaction mixture the corresponding (E) - 1 - iodoalk - 1 - ene **7** was also separated. (E) - 1 - Iodo - 3 - methylpent - 1 - ene, MS *m/e* (%) 210 (M^+), 181, 127, 83 (33), 55 (100), 54 (45), 53 (50), 41 (68), 39 (45), 29 (38), 27 (58); (E) - 1 - iodo - 3,4,4 - trimethylpent - 1 - ene, IR (neat) 1605, 685 cm^{-1}, MS *m/e* (%) 238 (M^+), 181 (6), 127 (7), 111 (11), 97 (9), 85 (28), 84 (13), 83 (20), 71 (14), 69 (23), 57 (100), 55 (14).

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