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SYNTHESIS AND CHIROPTICAL PROPERTIES OF SOME ASYMMETRIC PLANAR CISOID DIENES[a]

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Abstract—The synthesis and CD spectra of (+)-5α-androsta-14,16-diene (**2**), (−)-borno[2,3-*b*]cyclopenta-1,3-diene (**3**), (+)-2,3-dimethylenebornane (**4b**), (−)-borno[2,3-*c*]-2,5-diphenylcyclopenta-2,4-dien-1-one (**9a**), and related compounds are reported. A significant role is attributed to substituent chirality effects in these comparatively rigid, essentially planar cisoid conjugated diene systems.

Despite considerable investigation, the influence and bearing of structural and stereochemical features on the $\pi \rightarrow \pi^*$ Cotton effects of optically active conjugated dienes are still imperfectly understood. Inherent chiral disymmetry of the chromophore,[1] twisting of the individual double bonds,[2] and substituent bond chirality contributions[3] have all been assigned roles in determining the sign and intensity of CD bands of asymmetric 1,3-dienes. Although the relative importance of these factors remains open to debate, the CD behavior of certain types of dienes, especially heteroannular cisoid ones, appears to be controlled to a significant extent by chirality contributions of allylic axial bonds.[3a,4]

In this connection, the CD properties of comparatively rigid, essentially planar cisoid conjugated dienes are of particular interest. An example of such a diene, judging from Dreiding stereomodels, occurs in 3β,17-diacetoxy-5,14,16-androstatriene (**1**), for which $\Delta\epsilon$ +7·54 at 265 nm has been recorded.[5] Dreiding models also indicate that the much more flexible 5,7-diene system in the 9,10-*syn* steroids pyro- and isopyrocalciferol might be nearly planar, but recent X-ray structure determinations reveal, respectively, a C-6–C-7 dihedral angle of +9·5°[6] and +7·8°[7] in these two compounds. Interestingly, the strong positive 270–280 nm CD bands of these two compounds ($\Delta\epsilon$ *ca.* +25 to +30) are approximately twice as intense as those of the less flexible 9,10-*anti* isomers ergosterol ($\Delta\epsilon$ −18) and lumisterol$_3$ ($\Delta\epsilon$ +15),[2a,4] both of which have slightly larger C-6–C-7 dihedral angles (−11° for a closely related analog of ergosterol[8] and +15·5° for lumisterol$_3$[9]).§ In the present report, we describe our studies on the synthesis and chiroptical properties of some comparatively rigid, essentially planar conjugated dienes, including the unsubstituted 14,16-androstadiene **2**, the bornocyclopentadiene **3**, and the dimethylenebornane **4b**.

Synthesis of diene **2** was achieved from 17β-hydroxy-5α-androstan-3-one by the sequence: Wolff-Kishner (Huang-Minlon) reduction, oxidation to the 17-one, *p*-toluenesulfonylhydrazone formation, base-catalyzed conversion to 5α-androst-16-ene, allylic bromination, and dehydrobromination. Owing to the presence of a persistent brominated by-product, diene **2** was difficult to purify and was obtained only as a semi-solid with λ_{max} 262 nm (ϵ 4,200). The lowest-energy CD band was centered at 260 nm with $\Delta\epsilon$ +6·95, indicating that in **1** the 17-acetoxy group makes only a minor contribution to the 265 nm CD band.

Diene **3**, containing what is probably an essentially planar cisoid diene system that is both endocyclic and exocyclic, was produced from (−)-camphorquinone (2,3-bornanedione, **4a**) by reaction with the bis-Wittig reagent generated from 1,3-trimethylene-bis-triphenylphosphonium dibromide. The yield, however, was rather low (10%). On the other hand, the direct synthesis of diene **4b** by reaction of dione **4a** with 2 mols of methylenetriphenylphosphorane was unsuccessful. Reaction of **4a** with an excess of carbomethoxymethylenetriphenylphosphorane was successful but gave the known camphorylideneacetic acid derivative **4c**[10] instead of the desired dienic diester.

A satisfactory route to diene **4b** was ultimately achieved starting from the dimethylbornanediol **5a**. Obtained by addition of the methyl Grignard reagent to dione **4a**,[11] this glycol is assigned the *cis-exo* diol configuration by analogy with the formation of the *cis-exo* diol **5b** by LAH reduction of **4a**.[12] In the present work the *cis* configuration previously assigned[12,13] to the OH groups in **5a** and **5b** was further verified by a positive *cis*-glycol test (color discharge) with monopotassium triacetylosmate,[14] and the *exo*-diol assignment was supported by the effect of a lanthanide shift reagent on the NMR spectrum of **5a**.

By the method of Crank and Eastwood,[15] diol **5a** was converted into the cyclic orthoformate **6a**. The latter on heating gave (+)-2,3-dimethyl-2-bornene (**7a**), previously reported (with a small negative rotation) as a dehydration product of 3,3-dimethylborneol.[16] Application of the same sequence to diol **5b** furnished (−)-2-bornene (**7b**), but, as with **7a**, the final step required higher temperature and longer heating than reported[15] for the formation of less strained olefins. Besides having the expected spectral characteristics, olefin **7a** gave, by ozonolysis, (+)-*cis*-1,3-diacetyl-1,2,2-trimethylcyclopentane (**8**),[16] identical with that formed directly from **5a** by treatment with lead tetraacetate.[13] Efforts to prepare **7a** by heating the thionocarbonate of **5a** with triethyl phosphite[17] were unsatisfactory.

[a] Based on a presentation given at the 10*th Midwest Regional Meeting of the American Chemical Society*, Iowa City, Iowa, Nov. 7-8 (1974).

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‡Taken in part from the M.S. Thesis of N.C.N., The University of Kansas (1971).

§Unpublished temperature-dependent CD studies in these laboratories (with L. O. Weigel) indicate very little conformational mobility in any of these four steroidal 5,7-dienes.

Allylic bromination of olefin **7a**, followed by dehydrobromination, afforded, in 60% yield, an easily separated mixture of diene **4b** (84%) and recovered **7a** (16%). Alternatively, bis-allylic bromination of **7a**, followed by dehalogenation with zinc dust, also gave diene **4b** but in lower yield. Formation of polymer instead of diene has been observed in the dehalogenation of an analogous dichloro derivative in the norbornane series.[18]

Dienes **3** and **4b** were characterized by their distinctive spectral features and by formation of Diels-Alder adducts. In the UV, diene **3** exhibits typical cyclopentadiene absorption, centered at 242 nm (ϵ 5200). Diene **4b**, on the other hand, absorbs much more intensely with λ_{max} 248 nm (ϵ 10,100) and shoulders at 240 and 252 nm [*cf* 2,3-dimethylenenorbornane, λ_{max} 248 nm (ϵ 10,800)[19]]. The CD spectra (Fig. 1) of **3** and **4b** are, however, quite similar; both display comparatively weak negative bands in the 240–250 nm region, together with somewhat stronger positive ones near 200–210 nm.

In contrast to dienes **3** and **4b**, enones **4c**, **4d** and **4e** exhibit fairly intense positive $\pi \rightarrow \pi^*$ Cotton effects in the 225–255 nm region. (+)-3-Methylene-2-bornanone (**4d**), for example, is reported[20] to have a strong positive CD band (in cyclohexane) at 225 nm ($\Delta\epsilon$ +8·5) and an even stronger negative one near 195 nm ($\Delta\epsilon$ −14). Similarly, (+)-3-carbomethoxymethylene-2-bornanone (**4c**) was found in the present work to have a strong positive CD band (in hexane) at 240 nm ($\Delta\epsilon$ +12·6) and a negative one at 206 nm ($\Delta\epsilon$ −10·6). On the other hand, dione **4a** has a negative CD band (in cyclohexane[20] or hexane[1k]) at 222 nm ($\Delta\epsilon$ −1·3), a positive one at 204 nm ($\Delta\epsilon$ +1·0), and another negative one at 193 nm ($\Delta\epsilon$ −1·5). Clearly, the replacement of carbon by oxygen in these bornane derivatives causes the CD behavior, especially of the $\pi \rightarrow \pi^*$ transition, to change dramatically, even though the geometry of the chromophore is probably essentially unaltered.

For additional comparison, the deep red dienone **9a** was prepared by condensation of dione **4a** with 1,3-diphenyl-2-propanone. Like tetraphenylcyclopentadienone, **9a** apparently exists exclusively as a monomer. In the visible region it exhibits a weak negative CD band (in hexane) at 460 nm ($\Delta\epsilon$ −0·27) and a group of stronger positive bands in the 400-nm region. In the ultraviolet it has a strong negative CD band at 265 nm. Evidently for steric reasons, dienone **9a** did not undergo Diels-Alder cycloaddition even with tetracyanoethylene.[21] Unlike **9a**, the expected condensation product **9b** of dione **4a** with 3-pentanone appears to be mostly dimeric.

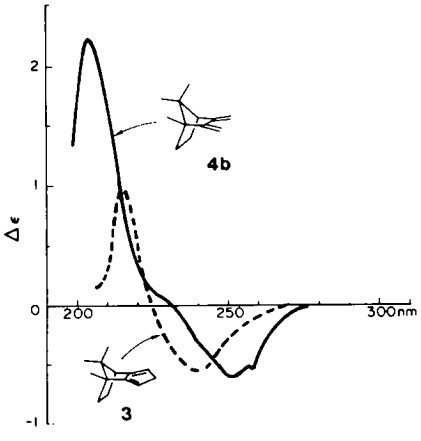

Fig. 1. CD spectra (in hexane) of (−)-borno[2,3-*b*]cyclopenta-1,3-diene (**3**) and (+)-2,3-dimethylenebornane (**4b**).

Incidental to these studies, we also re-examined the Claisen rearrangement of (+)-3-allyloxymethylene-2-bornanone (**4e**). As reported earlier for the rearrangement of racemic **4e**,[22] we found that both possible isomeric products, **10a** and **10b**, are formed, but with a substantial predominance of **10a**, as would be expected on steric grounds.[23] The chiroptical properties of these products are presented and discussed below.

DISCUSSION

For the conjugated bornane systems in the present study, chirality contributions from nonplanarity of the chromophore or from twisting of the individual double bonds are probably fairly small. (−)-Camphorquinone (**4a**), for example, has been shown by X-ray analysis to have only a slight positive (right-handed) dione chirality (+0·1° and +2·9°) in the crystalline state.[24] If this same skewness is present in the closely related dienes **3** and **4b**, then it is opposite in sign to their negative long-wavelength Cotton effects. In our view, therefore, the weak negative 240–250 nm $\pi \rightarrow \pi^*$ CD bands of **3** and **4b** are attributable to the overriding allylic bond polarization[3f] of the C-1–C-10 bond, making the left-handed (negative) chirality contribution of the allylic "axial" C-1–C-6 bond to the C-2 unsaturation dominant over the right-hand (positive) one from the C-4–C-5 bond to the C-3 unsaturation.[4,25] Similarly, in the case of enones **4c–e**, the positive $\pi \rightarrow \pi^*$ CD bands at 225–255 nm can be correlated with the positive allylic chirality contribution of the C-4–C-5 bond to the adjacent C=C double bond, whereas the negative $n \rightarrow \sigma^*$ (?) CD bands near 200 nm appear to be controlled by the negative chirality contribution of the C-1–C-6 bond to the adjacent carbonyl group.[4,25]

By contrast, (−)-2-bornene (**7b**), (+)-2,3-dimethyl-2-bornene (**7a**), and (−)-2-methyl-2-bornene (**7c**) all show a substantial negative Cotton effect in the 200–230 nm region, suggesting that an endocyclic double bond in this system, even when it bears an aryl group in the 2-position,[26] is dominated by a combination of negative chirality contributions from the C-4–C-5 and C-1–C-10 bonds. Compound **7c** was formed, together with **7b** and (−)-2-methylenebornane (**11a**), by treatment of (+)-camphor *p*-toluenesulfonylhydrazone with methyllithium and then methyl iodide.[27]

(−)-2-Methylenebornane (**11a**), like (−)-camphene (**11b**), exhibits a negative Cotton effect ($\Delta\epsilon$ −4·4[3f]) near 200 nm, in agreement with the expected dominant negative chirality contribution of the C-1–C-6 bond to the exocyclic double bond. The much greater intensity ($\Delta\epsilon$ −22) of the corresponding CD band of pure **11b** (prepared in connection with another problem[28]) suggests competing chirality contributions[3d] in **11a** from the C-7–C-8 and C-1–C-10 bonds to methyl groups, which, of course, are absent in **11b**.

A further point for consideration is why the long-wavelength $\pi \rightarrow \pi^*$ CD bands of the steroidal dienes **1** and **2** are so much more intense than those of the two bornane-series dienes **3** and **4b**. Molecular models suggest that the diene system in **1** and **2** is probably not quite planar but slightly bowed, with the substituents at C-14 and C-17 apparently being bent slightly below the plane of the diene toward the α side of the molecule. If true, this would lead to a slight twisting of the individual double bonds, but since this twisting would be enantiomeric, we conclude that the nature and degree of asymmetric

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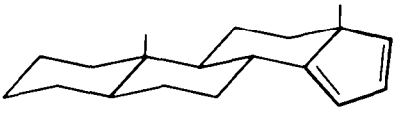

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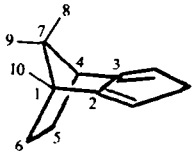

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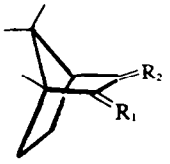
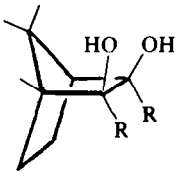
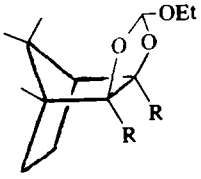


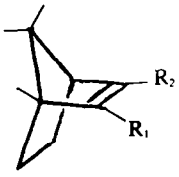
4a: $R_1 = R_2 = 0$
b: $R_1 = R_2 = CH_2$
c: $R_1 = O$, $R_2 = CHCO_2Me$
d: $R_1 = 0$, $R_2 = CH_2$
e: $R_1 = 0$; $R_2 = CHOCH_2CH{=}CH_2$



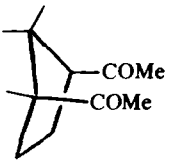
5a: R = Me
b: R = H



6a: R = Me
b: R = H



7a: $R_1 = R_2 = Me$
b: $R_1 = R_2 = H$
c: $R_1 = Me$, $R_2 = H$



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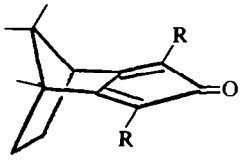
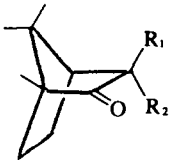
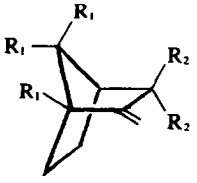


9a: R = Ph
b: R = Me



10a: $R_1 = CHO$, $R_2 = CH_2CH{=}CH_2$
b: $R_1 = CH_2CH{=}CH_2$, $R_2 = CHO$
c: $R_1 = CHO$, $R_2 = CH_2CH_2CH_3$



11a: $R_1 = Me$, $R_2 = H$
b: $R_1 = H$, $R_2 = Me$

substitution of the diene moiety compared to **3** and **4b** largely account for the stronger Cotton effect exhibited by **1** and **2**. The positive sign of this Cotton effect can be attributed, at least in part, to the net positive chirality contributions of the C-8β-H and C-13β-Me bonds to the 14–15 and 16–17 double bonds, respectively.[4]

Finally, it remains to consider the chiroptical properties of the Claisen rearrangement products **10a** and **10b**. In agreement with its negative 1,3-dione chirality, **10a**, together with its dihydro derivative **10c**, exhibits a negative 320-nm region $n \rightarrow \pi^*$ CD band (in hexane), whereas **10b**, with a positive 1,3-dione chirality, displays a positive band in this region.[29] Furthermore, as would be expected in relation to the sign of the $n \rightarrow \pi^*$ CD band,[30] the 200-nm region $n \rightarrow \sigma^*$ (?) CD band of **10a** and **10c** is positive, whereas that of **10b** is negative. In the intermediate 220–260 nm region, however, both **10a** and **10b** have positive CD bands, the stronger ones belonging to **10a** (right-handed 1,4-enone chirality) and the weaker ones to **10b** (left-handed 1,4-enone chirality). An underlying positive Cotton effect for **10a** in this region is indicated by the positive 224-nm CD band of its dihydro derivative **10c**. This suggests a dominance by positive chirality contributions to the ketone group from the C-1–C-10 and possibly the C-7–C-8 and C-4–C-5 bonds[3d] for this transition.

EXPERIMENTAL

Pet ether refers to petroleum distillates with b.p. 30–45°. M.ps were determined in open capillaries and, like b.ps, are uncorrected. IR spectra were recorded on a Perkin Elmer 137B Infracord spectrophotometer. UV spectra were measured with a Cary 14 recording spectrophotometer. CD and optical rotation data were determined on a Cary 60 recording spectropolarimeter equipped with a model 6001 CD assessory unit. NMR spectra were taken on a Varian T-60 instrument with TMS as internal reference. Gas chromatographic analyses and preparative separations were conducted on a Varian Aerograph gas chromatograph model A90-P3 fitted with a 1·85-m × 6·35-mm column packed with 10% Apiezon L on 60–80 Chromosorb W. Relative retention times (R_t) on this column are reported with reference to camphorquinone (**4a**) taken as 1. Elemental analyses were determined on an F&M-185 CHN analyzer by Mr. James Haug or Dennis Eisele, University of Kansas Department of Medicinal Chemistry. Mass spectra were obtained at 70 eV with a Varian MAT CH-5 spectrometer by Mr. Robert Drake, University of Kansas Department of Chemistry. Fragmentation patterns of compounds in the bornane series parallel those reported for camphor.[31]

5α-Androsta-14,16-diene (**2**). 5α-Androstan-17β-ol, m.p. 165–167° (lit.[32] 164°), was prepared in 92% yield from 17β-hydroxy-5α-androstan-3-one (Sigma Chemical Co., m.p. 180–182°) by Huang-Minlon reduction.[33] The 3,5-dinitrobenzoate (formed overnight at 25° in THF-pyridine with 3,5-dinitrobenzoyl chloride) crystallized from acetone-benzene as light tan needles (72%), m.p. 200–202°; NMR ($CDCl_3$) δ 0·83 (3 H, s), 0·98 (3 H, s), 4·89 (1 H, m), 9·06 (3 H, m); MS *m/e* (%) 470 (4, M^+), 258 (100). (Found: C, 66·36; H, 7·40; N, 5·67. $C_{26}H_{34}N_2O_6$ requires: C, 66·36; H, 7·28; N, 5·95%). The *β-naphthoate* (prepared during 10 hr of reflux in THF-pyridine with β-naphthoyl chloride) similarly crystallized from acetone-benzene but as colorless needles, m.p. 183–184°; $[\alpha]_D$ + 74° (hexane); NMR ($CDCl_3$) δ 0·84 (3 H, s), 0·97 (3 H, s), 4·88 (1 H, m), 7·4–8·1 (7 H, m); MS *m/e* (%) 430 (11, M^+), 155 (100). (Found: C, 83·57; H, 8·96. $C_{30}H_{38}O_2$ requires: C, 83·67; H, 8·89%).

Since efforts to prepare 5α-androst-16-ene by pyrolysis of the foregoing esters were unsatisfactory, an alternative route was employed. 5α-Androstan-17β-ol (800 mg) was oxidized by $Na_2Cr_2O_7$–H_2SO_4 aq in ether-THF by the method of Brown[34] at 25° for 20 min. Recrystallization (MeOH) of the neutral product isolated by extraction with ether afforded 710 mg (89%) of 5α-androstan-17-one as white platelets, m.p. 121° (lit.[35] 121·5–122°). This ketone (655 mg) was allowed to stand in 45 ml of dry MeOH with *p*-toluenesulfonylhydrazide (495 mg) and 3 drops of conc. HCl for 72 hr. Crystallization of the resulting *p*-toluenesulfonylhydrazone from MeOH gave colorless needles, m.p. 200–202° dec; NMR ($CDCl_3$) δ 0·78 (3 H, s), 0·82 (3 H, s), 2·4 (3 H, s), 7·0–8·0 (4 H, m); MS *m/e* (%) 442 (<1, M^+), 287 (100). (Found: C, 70·41; H, 8·67; N, 6·12. $C_{26}H_{38}O_2N_2S$ requires: C, 70·55; H, 8·65; N, 6·33%). After removal of MeOH, the *p*-toluenesulfonylhydrazone (*ca.* 1·06 g, 2·4 mmols) obtained directly from the preparation reaction was dissolved in 25 ml of dry THF and treated dropwise, with stirring at 5°, with 7·15 ml of 1·35 M MeLi (9·65 mmols) in THF under N_2.[36] Stirring was continued for 30 min at 20° and then for 1·5 hr at 40°. Following cautious addition of an equal vol of water to the deep red soln, stirring was continued for 10 min, and the mixture was extracted with pet ether. The organic layer was washed with water, dried ($MgSO_4$), concentrated, and the product eluted with pet ether from neutral alumina (1 × 10 cm). Crystallization from MeOH gave 500 mg (81%) of 5α-androst-16-ene as colorless plates, m.p. 78°, $[\alpha]_D$ + 20° (hexane) [lit.[37] m.p. 78–79°, $[\alpha]_D$ + 18° (EtOH)].

For conversion into diene **2**, the preceding product (100 mg) was heated at reflux for 20 min in 70 ml of dry CCl_4 with freshly recrystallized N-bromosuccinimide (82 mg) and dibenzoyl peroxide (10 mg).[38] The mixture was cooled, concentrated to 5 ml under reduced pressure, and the succinimide separated by filtration. After removal of the remaining CCl_4 the residue was dissolved in 5 ml of dry t-BuOH and added to 10 ml of a warm soln of t-BuOK in t-BuOH prepared from 0·2 g of K. The soln was refluxed for 2·5 hr, cooled, diluted with 150 ml of water, and extracted with pet. ether. The organic layer was washed well with water, dried ($MgSO_4$), concentrated, and the product eluted with pet. ether from neutral alumina (1 × 8 cm). Analysis by TLC (silica gel, hexane) revealed three major components: desired diene **2** (R_f 0·62), a bromodiene (R_f 0·69), and starting 5α-androst-16-ene (R_f 0·76).

Partial purification of diene **2** was achieved by preparative TLC and, more satisfactorily, by column chromatography on silica gel under pressure with hexane as eluent. Purified **2** was obtained as a semisolid oil, $[\alpha]_D$ + 209° (hexane); UV λ_{max} (hexane) 262 nm (ϵ 4,200); CD (hexane) 260 nm ($\Delta\epsilon$ + 6·85); NMR (CCl_4) δ 0·90 (3 H, s), 1·0 (3 H, s), 5·73 (1 H, m), 6·18 (2 H, m); MS *m/e* (%) 256 (47, M^+), 147 (100), 146 (42), 145 (26), 121 (32), 105 (42), 93 (32), 91 (47), 67 (26), 57 (26), 55 (32), [334 (1), 336 (1), corresponding to trace amounts of monobromo diene]. Although fairly stable in cold soln, **2** when isolated rapidly turns yellow and could not be made to give a satisfactory combustion analysis.

(−)-Borno[2,3-b]cyclopenta-1,3-diene [(4S, 7R)-4,8,8-*trimethyl*-2H,4,5,6,7-*tetrahydro*-4,7-*methanoindene*] (**3**). Oxidation of (+)-camphor with SeO_2 in Ac_2O gave improved yields (90%+) of pure (−)- **4a**, m.p. 199–200°, when the reaction time was extended from the reported 3–4 hr[39] to 12–15 hr. For the Wittig reaction, phenyllithium prepared from 7·85 g (0·05 mol) of bromobenzene and 0·7 g of Li (0·10 mol) in ether was added under argon to a stirred suspension of 13·0 g (0·02 mol) of 1,3-trimethylene-bis-triphenylphosphonium dibromide[40] in 100 ml of refluxing ether. After the reddish-brown mixture had stirred for 2 hr, 3·0 g (0·018 mol) of **4a** in 30 ml of dry ether was slowly added, and the mixture was refluxed overnight. Dry THF (20 ml) was introduced and the mixture heated for 6 hr as the ethyl ether was allowed to escape. The mixture was then stirred into ice-cold 2% HCl aq and the product recovered by extraction with pet. ether. After washing with water, 5% Na_2CO_3 aq, drying ($MgSO_4$), and concentration, the extracts were passed three times through neutral alumina (1·5 × 12 cm) with pet. ether to remove residual biphenyl, yielding *ca.* 0·32 g (10%) of crude diene **3**, b.p. (short-path) 90–100° (20 mm). An analytical sample collected by preparative gas chromatography (column temp 140°, R_t 0·465) was liquid at room temp., $[\alpha]_D$ − 0·4° (hexane); IR (CS_2) 5·9, 6·1, 6·2, 10·4, 11·15, 12·2, 13·0 μm; UV λ_{max} (hexane) 241 nm (ϵ 5,200); CD (hexane) 240 ($\Delta\epsilon$ − 0·55), 215 nm (+0·96); NMR (CCl_4) δ 0·68 (3 H, s), 0·95 (3 H, s), 1·12 (3 H, s), 1·1–2·0 (4 H, M), 2·43 (1 H, M), 3·01 (2 H, b), 5·59 (2 H, m); MS *m/e* (%) 174 (20, M^+), 159 (49), 131 (100), 117 (22), 91 (29). (Found: C, 89·52; H, 10·05. $C_{13}H_{18}$ requires: C, 89·59; H, 10·41%.)

On standing overnight at 20° with N-phenylmaleimide in

benzene, diene **3** formed a colorless adduct which crystallized from pet. ether-benzene as fluffy white crystals, m.p. 183–184°; NMR (CCl_4) no olefinic protons. (Found: C, 79·66; H, 7·52; N, 3·91. $C_{23}H_{25}NO_2$ requires: C, 79·51; H, 7·25; N, 4·03%).

(+)-2,3-*Dimethylenebornane* (**4b**). A soln of **7a** (1·0 g; 6·1 mmols) (see below) and freshly recrystallized N-bromosuccinimide (1·18 g; 6·6 mmols) in 100 ml of dry CCl_4 was heated briefly under a UV sunlamp and then refluxed without irradiation for 13 min, at which point HBr evolution began to be noticeable.[41]

The mixture was cooled, concentrated, and the succinimide collected before removal of the remaining CCl_4. The residue was dissolved in 25 ml of dry t-BuOH containing 12·3 mmols of t-BuOK and the mixture refluxed with magnetic stirring for 2 hr. After cooling, the mixture was diluted with 150 ml of water and extracted with pet. ether. The organic layer was washed well with water, dried ($MgSO_4$), concentrated, and the product eluted with pet. ether from neutral alumina (1·5 × 15 cm) yielding 0·60 g (60%) of crude hydrocarbon. GC analysis (130°) indicated the presence of 84% diene **4b** (R_f 0·25) and 16% starting olefin **7a** (R_f 0·156), making the overall yield of diene **4b** *ca* 50%. Separation of **4b** from **7a** was readily achieved by chromatography on $AgNO_3$-impregnated (10%) alumina;[42] **7a** was eluted with pet. ether, and diene **4b** was eluted with 1:9 ether-pet. ether. An analytical sample of diene **4b** obtained by preparative GC was a colorless liquid, $[\alpha]_D$ + 17° (hexane); IR (CCl_4) 6·05, 6·13, 11·3 μm; UV λ_{max} (hexane) 258 (sh) (ϵ 5,800), 248 (10,100), 240 (sh) nm (9,000); CD (hexane) 260 ($\Delta\epsilon$ − 0·53), 252 (−0·61), 204 nm (+2·2); NMR (CCl_4) δ 0·73 (3H, s), 0·93 (3H, s), 0·98 (3H, s), 2·20 (1H, m), 4·60, 4·70, 5·09, 5·11 (4 olefinic H's); MS *m/e* (%) 162 (8, M^+), 147 (20), 91 (24), 31 (100), 29 (55). (Found: C, 88·97; H, 10·94. $C_{12}H_{18}$ requires: C, 88·82; H, 11·18%). Reaction of olefin **7a** with 2·2 equiv of N-bromosuccinimide, followed by stirring for 3 hr with activated zinc dust, also afforded diene **4b** but in only 10–20% yield.

On warming in benzene with tetracyanoethylene, diene **4b** formed an off-white adduct which crystallized from benzene-pet. ether as small platelets, m.p. 207–208°; NMR ($CDCl_3$) no olefinic hydrogens; MS *m/e* (%) 290 (8, M^+), 134 (100). (Found: C, 74·57; H, 6·38; N, 19·56. $C_{18}H_{18}N_4$ requires: C, 74·46; H, 6·25; N, 19·29%).

(+)-3-*Carbomethoxymethylene*-2-*bornanone* (**4c**). A mixture of **4a** (166 mg; 1·0 mmol) and carbomethoxymethylenetriphenylphosphorane[43] (688 mg; 2·0 mmols) was heated under N_2 at 110° for 12 hr in a sealed tube. Afterward the mixture was digested with pet. ether and filtered. The filtrate was evaporated and the residue passed through neutral alumina (1 × 10 cm, activity grade III) with 1:1 pet. ether-ether. Evaporation of the solvents and microdistillation of the residue afforded 180 mg of a light yellow oil, b.p. (bath temp) 90–95° (1 mm), which slowly crystallized on standing at 0°. Recrystallization from MeOH aq gave 85 mg (39%) of **4c** as nearly colorless stout prisms, m.p. 59–61°, (lit.[10] 62–63°), $[\alpha]_D$ + 167° (hexane); IR (CCl_4) 5·73, 5·80, 6·0, 7·2, 7·3, 7·4, 8·2, 8·3, 8·5, 9·4, 9·9, 10·35 μm; UV λ_{max} (hexane) 243 nm (ϵ 13,400); CD (hexane) 240 ($\Delta\epsilon$ + 12·1), 206 nm (−10·6); NMR (CCl_4) δ 0·80 (3 H, s), 0·98 (3 H, s), 1·02 (3 H, s), 1·2–1·8 (4 H, m), 3·6 (1 H, m [deshielded C–4 $H^{\alpha+}$]), 3·70 (3 H, s), 6·28 (1 H, s); MS *m/e* (%) 222 (5, M^+), 194 (38), 179 (38), 139 (52), 83 (40), 55 (61), 41 (96), 28 (100). (Found: C, 70·52; H, 8·20. $C_{13}H_{18}O_3$ requires: C, 70·24; H, 8·16%).

(−)-3-*Allyloxymethylene*-2-*bornanone* (**4e**) was prepared in 65% yield from (+)-3-hydroxymethylene-2-bornanone[45] as described previously for the (±)-form.[22] The major fraction had b.p. 160–163° (2 mm), $[\alpha]_D$ (ether) + 155°; IR (CCl_4) 5·79, 6·05, 9·05, 10·1, 10·8 μm; UV λ_{max} (cyclohexane) 256 nm (ϵ 13,600); CD (hexane) 254 ($\Delta\epsilon$ + 7·9), 205 nm (−2·1); NMR (CCl_4) δ 0·78 (3 H, s), 0·87 (3 H, s), 0·90 (3 H, s), 1·3–2·1 (4 H, m), 2·78 (1 H, d, 5 Hz), 4·45 (2 H, m), 5·1–6·1 (3 H, vinyl multiplet), 7·0 (1 H, s).

(−)-2-endo, 3-endo-*Dimethylbornane*-2-exo, 3-exo-*diol* (**5a**). Reaction of **4a** (20·0 g; 0·12 mol) with an excess of MeMgI as described by Forster[11] furnished 12·0 g (50%) of pure **5a**, m.p. 132–133° $[\alpha]_D$ + 2° (EtOH). No improvement in yield occurred with MeLi. Diol **5a** discharged the blue color of monopotassium triacetylosmate, as expected for a cis glycol.[14] With increasing concentrations of Euroshift F (Pierce Chemical Co.), the NMR spectrum ($CDCl_3$) showed greater downfield shifts of the 3 Me peaks at δ 0·89, 1·15 and 1·30 than the 2 peaks at δ 0·88 and 1·28, which is consistent with a *cis-exo*-diol configuration.[46]

(−)-*Bornane*-2-exo, 3-exo-*diol* (**5b**). LAH reduction of **4a** (8·0 g; 0·048 mol) as described by Angyal and Young[12] afforded 7·6 g (94%) of **5b**, m.p. 256–258°, $[\alpha]_D$ − 18° (EtOH) as reported.[12] The steam-distillation step was found unnecessary. Like diol **5a**, **5b** also gave a positive test for a *cis* glycol with monopotassium triacetylosmate.[14]

(−)-2,3-*Dimethyl*-2-*bornene* (**7a**). Preparation of **6a** by exchange-reaction of **5a** (15·0 g, 0·076 mol) with ethyl orthoformate (11·3; 0·076 mol) in the presence of AcOH as catalyst at 130–145°[15] required 18 hr for liberation of 90% of the theoretical amount of EtOH. AcOH had to be added repeatedly as it slowly distilled from the reaction. An analytical sample of **6a** crystallized from pet. ether in thick, transparent needles, m.p. 63–64° $[\alpha]_D$ −11° (hexane); IR (CCl_4) 8·4, 8·9, 9·25, 9·6, 10·0, 10·1 μm; NMR (CCl_4) δ 0·83 (3 H, s), 0·89 (3 H, s), 1·15 (3 H, s), 1·22 (3 H, t, J = 7 Hz), 1·26 (3 H, s), 1·29 (3 H, s), 3·60 (2 H, q, J = 7 Hz), 5·44 (1 H, s), MS *m/e* (%) 254 (0·27, M^+), 180 (54), 165 (87), 137 (68), 124 (60), 109 (62), 95 (54), 43 (100). (Found: C, 70·69; H, 10·57. $C_{15}H_{26}O_3$ requires: C, 70·83; H, 10·30%).

Further heating of **6a** at 155–180° for 60 hr slowly liberated a third molar equivalent of EtOH. The pot residue was then distilled under reduced pressure, and the product with b.p. 60–100° (10–15 mm) was collected. Redistillation yielded 8·6 g (69% from diol **5a**) of analytically pure (+)- **7a**, b.p. 84–88° (30 mm), 176–178° (750 mm), $[\alpha]_D$ + 16° (hexane); n_D^{26} 1·4679; [lit.[16] for **7a** (?), b.p. 192–193°, $[\alpha]_D^{19}$ −5·76°, n_D^{25} 1·4765]; R_f 0·156; IR (CCl_4) 7·25, 7·35, 8·85, 11·3 μm; CD (hexane) 222 nm ($\Delta\epsilon$ −0·96); NMR (CCl_4) 0·73 (6 H, s), 0·91 (3 H, s), 1·49 (3 H, s) 1·61 (3 H, s), 1·97 (1 H, m); MS *m/e* (%) 164 (18, M^+), 149 (18), 136 (86), 121 (100), 107 (23), 105 (32), 91 (23). (Found: C, 87·55; H, 12·46; $C_{12}H_{20}$ requires: C, 87·73; H, 12·27%).

For structural verification, **7a** (0·9 g) in 50 ml CH_2Cl_2 was ozonized at −78° until the soln turned blue. After being flushed with N_2, the soln was stirred for 30 min under H_2 with 0·1 g of 10% Pd–C. Filtration and evaporation afforded a ketonic product with the same IR and NMR spectral characteristics as those obtained for the diketone **8** (see below) formed by $Pb(OAc)_4$ cleavage of diol **5a**.[13]

Hydrogenation of **7a** (1·0 g) in AcOH (20 ml) over prereduced PtO_2 (50 mg) required 3 hr for completion. Filtration, dilution with water, and extraction with pet. ether gave a mixture containing (by GC at 130°) 78% of one dihydro isomer (R_f 0·26) and 22% of another (R_f 0·38). By preparative GC the major product, tentatively identified as (−)-2-*exo*,3-*exo*-dimethylbornane, was obtained as a solid which melted slightly above room temp, $[\alpha]_D$ − 3° (hexane); IR (CCl_4) 6·78, 6·91, 7·22, 7·30 μm; MS *m/e* (%) 166 (3, M^+), 151 (15), 123 (56), 95 (76), 83 (21), 82 (100), 81 (27), 69 (21), 67 (33), 55 (48), 41 (27). (Found: C, 86·44; H, 13·62. $C_{12}H_{22}$ requires: C, 86·67; H, 13·33%). The minor product, possibly the (+)-2-*endo*,3-*endo*-isomer, was a liquid, $[\alpha]_D$ + 4° (hexane); IR (CCl_4) 6·79, 6·94, 7·21, 7·31 μm; MS *m/e* (%) 166 (2, M^+), 151 (20), 123 (50), 97 (21), 96 (24), 95 (100), 83 (55), 82 (100), 81 (38), 70 (24), 69 (64), 67 (45), 57 (38), 55 (89), 41 (70). (Found: C, 86·47; H, 13·53, $C_{12}H_{22}$ requires: C, 86·67; H, 13·33%).

The complex pattern of Me proton signals in the NMR spectra of these products occurs at δ 0·7–1·1.

Thionocarbonate of diol **5a**. By the method of Corey and Winter,[17] **5a** (1·98 g; 0·010 mol) afforded purified thionocarbonate (1·51 g; 63%), which crystallized from CH_2Cl_2-ligroin as colorless needles, m.p. 161–163°; $[\alpha]_D$ − 19° (EtOH); IR ($CHCl_3$) 7·65 μm; CD (hexane) 316 nm ($\Delta\epsilon$ − 0·09) [*cf* thionocarbonate of **5b**, CD (dioxane) 312 nm ($\Delta\epsilon$ − 0·08)[47]]; NMR (CCl_4) δ 1·01 (6 H, s), 1·19 (3 H, s), 1·42 (3 H, s), 1·51 (3 H, s), 2·1 (1 H, m). (Found: C, 64·81; H, 8·17. $C_{13}H_{20}O_2S$ requires: C, 64·96; H, 8·39%).

Prolonged refluxing of this derivative with triethyl phosphite[17] provided only trace amounts of olefin **7a**. The use of other reagents, such as bis(1,5-cyclooctadiene)nickel,[48] for this conversion was not investigated.

(−)-2-*Bornene* (**7b**) *from diol* **5b**. Ethyl orthoformate (4·75 g, 0·032 mol) and **5b** (5·45 g, 0·032 mol) were heated together at 140–145° in the presence of 100 mg mesitoic acid as catalyst. After 20 hr, 3·6 ml of EtOH (96% of the theoretical amount) had been

literated, and formation of **6b** was essentially complete according to the NMR (CCl_4) spectrum: δ 0·79 (3 H, s), 0·93 (3 H, s), 1·12 (3 H, s), 1·22 (3 H, t, J = 7 Hz), 3·50 (1 H, d, J = 7 Hz), 3·62 (2 H, q, J = 7 Hz), 3·80 (1 H, t, J = 7 Hz), 5·39 (1 H, s). Further heating of **6b** at 170° for 72 hr slowly liberated 1·7 ml of EtOH (91% of theory) as 3·3 g (76%) (−)-2-bornene (**7b**) crystallized on the walls of the condenser. Crystallization from MeOH afforded transparent prisms of chromatographically pure **7b**, m.p. 112·5° (lit.[49] 113°); R_f 0·087; CD (hexane) 202 nm ($\Delta\epsilon$ − 3·94).

(−)-2-*Methyl*-2-*bornene* (**7c**) (with David Bamberger). A magnetically stirred soln of (+)-camphor *p*-toluenesulfonylhydrazone (1·0 g; 3·1 mmols), m.p. 163–164°, in 10 ml dry THF was treated at 0° under N_2 with 6·9 mmols of MeLi in ether.[36] The resulting red soln was stirred at 20° for 4 hr, 1·5 g (10·6 mmols) of MeI was added,[27] and stirring was continued overnight. After careful addition of water to the mixture, the product isolated by extraction with pet. ether was passed through neutral alumina (1·5 × 15 cm). GC analysis (125°) indicated the hydrocarbon product was a mixture containing (−)- **7b** and (−)- **11a**, $[\alpha]_D$ − 45°,[50] R_f 0·165, CD (hexane) 203 nm ($\Delta\epsilon$ − 4·4[37]), as well as the desired (−)- **7c**, R_f 0·124, in the ratio 3:5:2, respectively, which was variable from several runs. An analytical sample of **7c**, obtained by preparative GC, was a fragrant liquid, $[\alpha]_D$ − 18° (hexane); CD (hexane) 205 ($\Delta\epsilon$ − 3·52); NMR (CCl_4) δ 0·78 (6 H, s), 0·93 (3 H, s), 1·61 (3 H, d, J = 2 Hz), 5·52 (1 H, m); MS *m/e* (%) 150 (24, M^+), 135 (34), 107 (98), 95 (46), 94 (64), 93 (72), 91 (52), 79 (96), 69 (30), 41 (100). (Found: C, 87·90; H, 12·12. $C_{11}H_{18}$ requires: C, 87·93; H, 12·07%).

(+)-cis-1,3-*Diacetyl*-1,2,2-*trimethylcyclopentane* (**8**). Diol **5a** (1·0 g, 5 mmols) and 85% $Pb(OAc)_4$ (3·0 g, 5·7 mmols) were dissolved in AcOH (20 ml) and the soln stirred at 20° for 10 min. After dilution with water, the mixture was extracted with ether, and the ether layer was washed with water, 5% NaOH aq, and dried ($MgSO_4$). Evaporation of the solvent afforded **8** (0·78 g; 80%) as a colorless oil, $[\alpha]_D$ − 123° (hexane) [lit.[16] for **8** (?) −6·87° and +38·9°], IR (CCl_4) 5·89, 7·2, 7·3, 7·4, 8·1, 8·6, 9·1, 9·2 μm; CD (hexane) 301 nm ($\Delta\epsilon$ + 7·30); NMR (CCl_4) δ 0·72 (3 H, s), 1·15 (3 H, s), 1·32 (3 H, s), 2·08 (6 H, s). The mono-2,4-DNP, m.p. 150–152°, crystallized from EtOH as large orange needles (together with the powdery yellow bis-2,4-DNP, from which it could be readily separated by hand); MS *m/e* (%) 376 (13, M^+), 333 (22), 109 (25), 55 (22), 43 (100). (Found: C, 57·04; H, 6·42; N, 15·17. $C_{18}H_{24}N_4O_5$ requires: C, 57·44; H, 6·43; N, 14·88%).

(−) *Borno*[2,3-c] - 2,5 - *diphenylcyclopenta* - 2,4 - *dien* - 1 - *one* [(4S,7R) - 1,3 - *diphenyl* - 4,8,8 - *trimethyl* - 2 H,4,5,6,7 - *tetrahydro* - 4,7 - *methanoinden* - 2 - *one*] (**9a**). Triethylene glycol (10 ml) containing **4a** (2·0 g; 12 mmols) and 1,3-diphenyl-2-propanone (2·53 g; 12 mmols) was heated to 100°, and 1·3 ml of benzyltrimethylammonium hydroxide (35% in MeOH) was added slowly.[51] The soln was heated overnight at 100° under N_2. After cooling, the dark red soln was diluted well with water and extracted with ether. The combined red ether extracts were washed with water, 5% HCl aq, 5% NaOH aq, satd NaCl aq, and dried ($MgSO_4$). Evaporation of the ether furnished a thick red oil which was passed rapidly through neutral alumina (1·5 × 20 cm) with pet. ether-benzene and then chromatographed on silica gel (1·5 × 20 cm) with 6:1 pet. ether-benzene as eluent. The desired **9a** was eluted first, followed by recovered **4a**. Crystallization of **9a** from pet. ether-benzene gave deep red platelets, m.p. 111–112°, $[\alpha]_D$ − 66° (hexane), −55° (THF); IR (CCl_4) 5·85, 6·13, 6·29, 6·71, 6·95, 7·22, 13·3, 14·4 μm; UV λ_{max} (hexane) 462 (ϵ 4,700), 255 nm (37,600); CD (hexane) 460 ($\Delta\epsilon$ − 0·26), 430 (+0·79), 407 (+1·45), 387 (+1·26), 265 nm (−9·26); NMR (CCl_4) δ 1·0 (3 H, s), 1·09 (3 H, s), 1·15 (3 H, s), 3·05 (1 H, m), 7·1–7·8 (10 H, m); MS *m/e* (%) 340 (100, M^+), 325 (83). (Found: C, 88·27; H, 7·26. $C_{25}H_{24}O$ requires: C, 88·19; H, 7·11%).

Efforts to obtain diene adducts from **9a** with tetracyanoethylene led only to recovery of starting material. Base-catalyzed condensation of 3-pentanone with **4a** led to dark colored products from which no pure substance could be isolated.

(−) *and* (+)-3-*Allyl*-3-*formyl*-2-*bornanone* (**10a** and **10b**, respectively) were prepared by heating **4e** to 210–220° in a sealed tube as described previously.[22] With slow heating to 210° the product ratio as determined by GC (180°) was 86:14; with rapid heating it was 75:25. The major product, identified as (−)-3-endo-*allyl*-3-exo-*formyl*-2-*bornanone* (**10a**), crystallized from the mixture and pet. ether at −20°. This had R_f 0·465, b.p. 121–125° (1 mm), m.p. 33–34°, $[\alpha]_D$ −103° (cyclohexane); IR (CCl_4) 3·68, 5·71, 5·80, 6·1, 7·20, 7·30, 10·0, 10·85 μm; CD (cyclohexane 319 ($\Delta\epsilon$ − 4·86), 3·09 (−4·14), 224 (+2·55), 200 nm (+5·24); NMR (CCl_4) δ 0·56 (3 H, s), 0·88 (3 H, s), 1·02 (3 H, s), 2·58 (2 H, m), 4·8–6·0 (3 H, m), 9·30 (1 H, s); MS *m/e* (%) 220 (25, M^+), 177 (60), 136 (50), 95 (55), 83 (95), 55 (95), 41 (100). (Found: C, 76·38; H, 9·28. $C_{14}H_{20}O_2$ requires: C, 76·33; H, 9·15%).

The minor product, designated as (+)-3-exo-*allyl*-3-endo-*formyl*-2-*bornanone* (**10b**), was a liquid, b.p. 121–125° (1 mm), R_f 0·80, $[\alpha]_D$ + 190° (cyclohexane); IR (CCl_4) 3·67, 5·71, 5·80, 6·05, 7·20, 7·30, 10·0, 10·8 μm; CD (cyclohexane) 314 ($\Delta\epsilon$ + 2·09), 255 (+1·15), 220 (+0·22), 204 nm (−5·13); NMR (CCl_4) δ 0·90 (3 H, s), 1·00 (6 H, s), 2·57 (2 H, m), 4·8–6·0 (3 H, M), 9·27 (1 H, s); MS *m/e* (%) 220 (9, M^+), 192 (19), 177 (41), 136 (42), 95 (52), 83 (94), 55 (100), 41 (86). (Found: C, 76·35; H, 9·13. $C_{14}H_{20}O_2$ requires: C, 76·33; H, 9·15%).

Hydrogenation of **10a** in EtOH over 10% Pd–C furnished the corresponding dihydro derivative, (−)-3-endo-*n*-*propyl*-3-*formyl*-2-*bornanone* (**10c**), m.p. 75–76°, $[\alpha]_D$ − 109° (hexane), which crystallized from pet. ether at −20°; CD (hexane) 320 ($\Delta\epsilon$ − 5·95), 309 (−5·33), 224 nm (+4·18). (Found: C, 75·62; H, 10·10. $C_{14}H_{22}O_2$ requires: C, 75·63; H, 9·97%).

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