Stereochemistry of 2-Benznorbornenone[1,2]

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Abstract: 2-Benznorbornenone (**1**), the simplest example of a conformationally rigid, dissymmetric β,γ-benzo ketone, has been prepared in optically active form by asymmetric hydroboration of benznorbornadiene (**2**), followed by oxidation of the resulting *exo*-2-benznorbornenol. The optical purity of **1**, its precursors, and its derivatives was determined from relative signal intensities in the nmr spectrum of the O-methylmandelate of (+)-*endo*-2-benznorbornenol, derived from (+)-**1**. The absolute configuration of (+)-**1** was assigned as 1*R* on the basis of three independent criteria: (a) a comparison of the inductions achieved in the asymmetric hydroboration of norbornene, norbornadiene, and **2**, (b) the direction of the asymmetric synthesis of *exo*-2-benznorbornenyl *p*-toluenesulfinate, and (c) the ORD and CD of **1**. In sign and magnitude the rotational strength of the intensified n $\rightarrow \pi^*$ transition of (+)-**1** is that expected for the relevant β,γ-unsaturated ketone chromophore. In the course of this work, it was found that reaction of a 1:1 adduct of (+)-α-pinene and $BH_3 \cdot THF$ with **2** gives either enantiomer of *exo*-2-benznorbornenyl acetate, depending on the time elapsed before the reagents are mixed. It is suggested that rearrangement and/or disproportionation of the initially formed adduct may play a role in the sign reversal.

The dissymmetric β,γ-benzo ketone chromophore, which occurs in a variety of natural products and derived substances,[4-7] is of special interest in connection with earlier studies of dissymmetric β,γ-unsaturated ketones, which dealt with the stereochemical requirements for the intensification of the optical rotatory power of the carbonyl n $\rightarrow \pi^*$ transition[8-10] and with the theoretical foundations[4,11] for the generalized octant rule.[4] The present work describes the preparation of (+)-**1**, the determination of its optical purity and absolute configuration, a discussion of its ORD and CD in relation to the earlier work cited above, and an anomaly in the stereochemistry of asymmetric hydroboration of olefins, which was encountered in the course of this work.

Syntheses. Direct entry into the optically active benznorbornenyl system was conveniently achieved by reaction of benznorbornadiene (**2**) with tetraisopinocampheyldiborane[12-14] (**3**) in diglyme[15] at 0°. When **2** was allowed to react with (−)-**3** derived from *ca.* 75% optically pure (+)-α-pinene (**4**) in diglyme for 3 hr at 0°, oxidized, and acetylated, the product was *exo*-2-benznorbornenyl acetate[16] (**5**), $[\alpha]^{25}D$ +31.7° (ethanol). Subsequent transformations leading to **1** were analogous to those previously described for the preparation of dehydronorcamphor:[9] lithium aluminum hydride reduction of (+)-**5** gave *exo*-2-benznorbornenol (**6**), $[\alpha]^{26}D$ +15.8° (chloroform), Oppenauer oxidation of which afforded (+)-**1**, $[\alpha]^{25}D$ +262° (isooctane). The identity of **6** as the *exo* diastereomer follows from comparison of its ir spectrum with that of *endo*-2-benznorbornenol (**7**),[17] which was prepared[18] by lithium aluminum hydride reduction of **1**: whereas **6** shows only a free O–H stretching frequency at 3623 cm^{-1}, **7** shows intramolecular hydrogen bonding to the benzene ring (OH stretch at 3576 cm^{-1}),[19] in addition to the free O–H stretch at 3624 cm^{-1} ($\Delta\nu$ 48 cm^{-1}), an observation which is consistent only with the *endo* configuration for **7**.[20,21]

Determination of Optical Purity. Discussion of the optical rotatory properties of (+)-**1** requires an accurate measure of the optical purity of the samples obtained

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[2] For a preliminary account of a portion of this work, see W. P. Giddings and J. Dirlam, *J. Amer. Chem. Soc.*, **85**, 3900 (1963).

[3] (a) National Aeronautics and Space Administration Fellow, 1965–1968; (b) National Science Foundation Undergraduate Research Participant.

[4] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).

[5] (a) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., B*, 215 (1967); (b) D. E. Bays and R. C. Cookson, *ibid.*, 226 (1967).

[6] S. F. Mason, *ibid.*, 3285 (1962).

[7] (a) R. C. Cookson and J. Hudec, *ibid.*, 429 (1962); (b) T. R. Hollands, P. de Mayo, M. Nisbet, and P. Crabbé, *Can. J. Chem.*, **43**, 3008 (1965); (c) P. Crabbé and A. Bowers, *J. Org. Chem.*, **32**, 2921 (1967), and references cited therein, especially ref 2, 8, 9, and 18; (d) P. Crabbé and W. Klyne, *Tetrahedron*, **23**, 3449 (1967); (e) J. P. Connolly, R. Ó. Dorchai', and J. B. Thomson, *J. Chem. Soc., C*, 461 (1968).

[8] K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962).

[9] K. Mislow and J. G. Berger, *J. Amer. Chem. Soc.*, **84**, 1956 (1962).

[10] (a) E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *ibid.*, **84**, 2823, 5003 (1962); (b) D. J. Sandman and K. Mislow, *J. Org. Chem.*, **33**, 2924 (1968).

[11] (a) A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolymers Symp.*, **1**, 75 (1964); (b) A. Moscowitz, *Proc. Roy. Soc.* (London), **A297**, 16, 40 (1967); (c) R. E. Ballard, S. F. Mason, and G. W. Vane, *Trans. Faraday Soc.*, **59**, 775 (1963).

[12] H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

[13] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

[14] D. R. Brown, S. F. A. Kettle, J. McKenna, and J. M. McKenna, *Chem. Commun.*, 667 (1967).

[15] Use of tetrahydrofuran (THF) in place of diglyme resulted in a product of considerably lower optical purity (see Experimental Section). A decrease in the stereoselectivity of asymmetric hydroboration accompanying a change of solvent from diglyme to THF had been previously observed[13] for *cis*-2-butene.

[16] A trace (*ca.* 1%) of the *endo* isomer (configuration and optical purity unknown) accompanied preparations of **5**.

[17] We thank Dr. L. Joris for these measurements (taken in dilute carbon tetrachloride solution).

[18] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

[19] For a review, see M. Tichý, "Advances in Organic Chemistry, Methods and Results," Vol. 5, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 115 ff.

[20] Bartlett and Giddings[18] assigned the *endo* configuration to **7** on mechanistic grounds.

[21] Similar arguments were recently employed in the assignment of configurations to the *exo* and *endo* isomers of 5,8-dimethoxy-2-benznorbornenol (H. Tanida, T. Tsuji, and S. Teratake, *J. Org. Chem.*, **32**, 4121 (1967)).

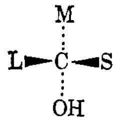
in the asymmetric hydroboration of **2**. An estimate of the optical purity was obtained by application of the nmr method, using derivatives of O-methylmandelic acid.[10b,22]

Reaction of a sample of **6**, $[\alpha]^{24}\mathrm{D}$ +0.7° (chloroform), with an equimolar quantity of racemic O-methylmandelyl chloride gave a mixture of diastereomers whose 60-MHz nmr spectrum in benzene solution indicated that the methoxymethine (CH_3O–C–*H*) and methoxy (CH_3O) protons were not perceptibly anisochronous. On the other hand, reaction of racemic **7** with an excess of optically pure (*R*)-O-methylmandelyl chloride gave a mixture of diastereomeric esters whose 60-MHz nmr spectrum in benzene solution showed signals for the diastereotopic methoxymethine protons which were separated by *ca.* 6 Hz, and signals for the diastereotopic methoxy protons which were separated by *ca.* 5 Hz; the diastereomeric ratio was 1:1, as judged by integration of either set of signals. Since this preparation of **7** was accompanied by 5% of **6**, it should be pointed out that both sets of signals for the diastereomers derived from **7** were well separated from those of the diastereomers derived from **6** and could therefore be safely used in the determination of optical purity.

A sample of (+)-**7**, $[\alpha]^{22}\mathrm{D}$ +39.1° (chloroform), prepared by lithium aluminum hydride reduction of (+)-**1** and containing 2% of **6**, was treated with optically pure (*R*)-O-methylmandelyl chloride. The product, *endo*-2-benznorbornenyl O-methylmandelate, consisted of a mixture of diastereomers in the ratio of 2.7:1.0, as judged independently either by integration of the methoxy or of the methoxymethine signals. Accordingly, the optical purity of precursors **5**, **6**, **1**, and **7** is established as (2.7 − 1.0)/(2.7 + 1) or 46%, and the absolute rotations as $[\alpha]\mathrm{D}$ +69° (ethanol), $[\alpha]\mathrm{D}$ +34° (chloroform), $[\alpha]\mathrm{D}$ +570° (isooctane), and $[\alpha]\mathrm{D}$ +84° (chloroform),[23] respectively.

Absolute Configurations. It had earlier been shown[9,24] that reaction of (−)-**3**, prepared from *ca.* 75% optically pure (+)-**4**, with norbornadiene and norbornene in diglyme gave 48% optically pure (+)-(1*R*,2*S*)-*exo*-dehydronorborneol (**8**) and (−)-(1*S*,2*S*)-*exo*-2-norborneol, respectively.[25] In the present work, reaction of (−)-3, prepared from *ca.* 75% optically pure (+)-**4**, with **2** in diglyme gave 46% optically pure (+)-**6**. Since the comparable asymmetric induction achieved in these three structurally similar systems presumably reflects analogous topographical features in the diastereomeric transition states leading to the optically active products, it is safe to conclude that (+)-**6** has the 1*R*,2*S* configuration. The absolute configurations of the related benznorbornenyl compounds (+)-**5**, (+)-**1**, and (+)-**7** are therefore 1*R*,2*S*, 1*R*, and 1*R*,2*R*, respectively.

This configurational assignment was confirmed in the following manner. It had previously been shown[26] that the asymmetric synthesis of *p*-toluenesulfinate esters from optically active alcohols and *p*-toluenesulfinyl chloride leads to an excess of one diastereomer, whose configuration, as determined by stereospecific conversion to methyl *p*-tolyl sulfoxide (**9**) with methylmagnesium iodide, can be related to that of the predominant enantiomer in the inducing alcohol by an empirical rule. This rule states that an alcohol corresponding to stereoformula **10** yields an excess of the (+)-*R* enantiomer of **9** in the asymmetric synthesis described.



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L = large group
M = medium-sized group
S = small group

Application of this method to a solution of the present problem was complicated by the uncertainty inherent in the identification of the L and M groups in **6** or **7** (given that S = H on C-2). While such uncertainty does not exist in dehydroisoborneol and dehydroborneol or the corresponding saturated alcohols,[26] the identification becomes less secure when the C-methyl groups are lacking. Consequently, it became necessary first to calibrate the method by use of an alcohol of closely related structure and of known absolute configuration. This was done by treating (1*R*,2*S*)-**8**,[9] $[\alpha]^{25}\mathrm{D}$ +6.8° (chloroform), *ca.* 57% optically pure, with *p*-toluenesulfinyl chloride at −78°. The resulting mixture of diastereomeric sulfinates was then allowed to react with methylmagnesium iodide, to give (+)-(*R*)-**9**, 2.7% optically pure. Accordingly, the L and M groups in **8** are identified with C-1 and C-3, respectively. When (+)-**6**, $[\alpha]^{23}\mathrm{D}$ +5.8° (chloroform), 17% optically pure, was allowed to react under the same conditions, (+)-**9**, 1.5% optically pure, was obtained. The regions near the reaction center (C-2) in **6** and **8** are closely similar, and C-1 and C-3 in **6** may therefore be identified as L and M groups, respectively. Since (+)-**6**, having given rise to (+)-**9**, corresponds to stereoformula **10**, it follows that (+)-**6** has the 1*R*,2*S* configuration.[27]

The relative chemical shifts of the methoxymethine protons in the (*R*)-O-methylmandelates derived from *endo*-dehydronorborneol (**11**)[10b] and from **7** are consistent with these configurational assignments. The signal of the methoxymethine proton in the diastereomer derived from the predominant enantiomer of **11**, (−)-(1*S*,2*S*)-**11**, is shifted *downfield* (by 4 Hz at 100 MHz) relative to the corresponding signal in the diastereomer derived from the minor enantiomer.[10b] On the other hand, the methoxymethine proton in the diastereomer derived from the predominant enantiomer of **7** is shifted *upfield* (by 6 Hz at 60 MHz) relative to the corresponding signal in the diastereomer derived from the minor enantiomer. Since the shielding of the

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(22) (a) M. Raban and K. Mislow, "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 216 ff; (b) M. Raban and K. Mislow, *Tetrahedron Lett.*, 3961 (1966); (c) J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.*, 33, 1142 (1968); J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, 90, 3732 (1968).

(23) Corrected for the presence of 2% of (+)-**6**.

(24) J. G. Berger, Ph.D. Thesis, New York University, 1962.

(25) Brown, *et al.*,[13] have reported that norbornene reacts with (−)-**3**, derived from (+)-**4** of 93–95% optical purity, in diglyme to give (−)-norborneol of 67–70% optical purity.

(26) M. M. Green, M. Axelrod, and K. Mislow, *J. Amer. Chem. Soc.*, 88, 861 (1966).

(27) The comparatively[26] low optical yields obtained in the asymmetric syntheses of the *p*-toluenesulfinates of **8** and **6** (5 and 9%, respectively, after correction to optical purity in the inducing alcohols) are evidence of the rather slight differences in effective size of the L and M groups in these systems.

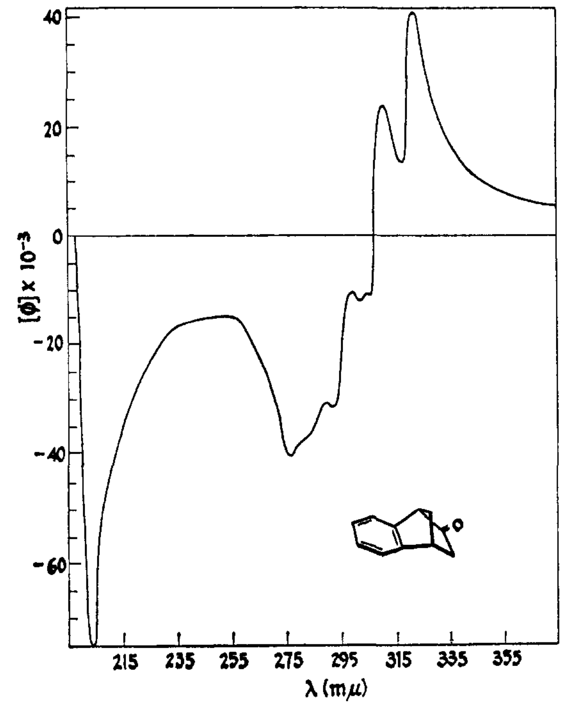

Figure 1. Optical rotatory dispersion of (+)-**1** in isooctane solution, corrected to optical purity.

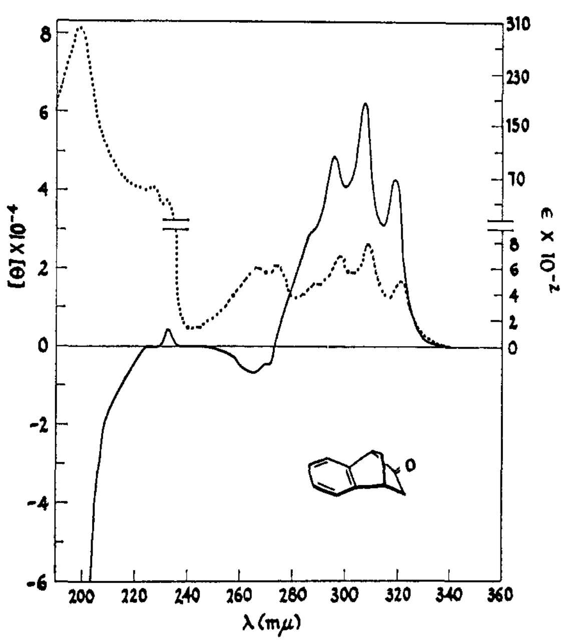

Figure 2. Circular dichroism (solid line) and absorption spectrum (dashed line) of (+)-**1** in isooctane solution. The molecular ellipticity is corrected to optical purity.

methoxymethine protons in the two esters in comparable,[28] the sense of chemical shift nonequivalence[29] in the esters derived from the predominant enantiomers is *opposite*, a result which is consistent with the assignment of the 1*R*,2*R* configuration to (+)-**7**. On the basis of the limited number of examples available to us,[30] it would, however, be premature to claim any generality for the relative position of the methoxymethine signal in diastereomeric O-methylmandelates or O-methylmandelamides.[30]

Optical Rotatory Power of (+)-2-Benznorbornenone and Related Compounds. The relevant optical data for (+)-**1** are displayed in Figures 1 and 2. The optical rotatory dispersion (ORD) in Figure 1 and the circular dichroism (CD) in Figure 2 clearly reveal the features of primary concern, *i.e.*, the sign, shape and intensity of the Cotton effect of the n → π* transition in the region 280–320 mμ. The positive sign reflects the chirality of the composite β,γ-benzo ketone chromophore which was established through the work described in the preceding section and which is depicted in the figures. The sign is in accord with the tenets of the generalized octant rule,[4] thus confirming the configurational assignment.

The shape of the ORD and CD curves is characteristic of related β,γ-unsaturated ketones.[4,8–10] The high rotational strength expected of such dissymmetric chromophores is reflected in the high molecular amplitude (*a* +840, corrected to optical purity) and molecular ellipticity ($[\theta]_{\max}$ +6.2 × 10^4 at 307.5 mμ corrected to optical purity) of the intensified n → π* transition; it is noteworthy that these values are higher than those observed for other β,γ-benzo ketones[4–7] in which the relative disposition of the benzene ring and carbonyl group is similar to that in **1**.

In addition to the n → π* transition, several other instrumentally accessible electronic transitions of (+)-**1** were found to be optically active. The CD curve (Figure 2) discloses the presence of two relatively weak Cotton effects at *ca.* 265 mμ ($[\theta]_{\max}$ −7.2 × 10^3, corrected to optical purity) and at *ca.* 232 mμ ($[\theta]_{\max}$+4 × 10^3, corrected to optical purity), and the beginnings of a strong negative Cotton effect centered below 210 mμ. The position and intensity of the absorption associated with the 265-mμ Cotton effect, when compared to those of other benznorbornenyl derivatives,[18,32] suggest that it may be assigned to the $B_{2u} \leftarrow A_{1g}$ benzenoid transition; such transitions are predicted[33] to have low rotational

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(28) The O-methylmandelates of **6** and **8**[10b] do not exhibit perceptible (in benzene at 60 MHz) chemical shift differences in the diastereotopic methoxy or methoxymethine proton resonances, in contrast to the methoxymethine signals of **7** and **11** and the methoxy signals of **7**. It appears that the differential shielding experienced by the protons in the *endo* isomers is traceable to the over-all shielding of the protons in question, relative to the corresponding protons in the *exo* isomers. Thus, the diastereotopic methoxymethine proton signals in **7** are 13 and 19 Hz upfield of the coincident signals in **6**, the diastereotopic methoxy proton signals in **7** are 5 and 10 Hz upfield of the coincident signals in **6**, the diastereotopic methoxymethine proton signals in **11** are 3.5 and 5.5 Hz upfield of the coincident signals in **8**,[10b] and the coincident methoxy signals in **11** are *ca.* 1 Hz upfield of those in **8**,[10b] all at 60 MHz in benzene. These phenomena may be ascribed to the anisotropy of the olefin (in **11**) or benzene (in **7**) π system, which is conformationally accessible to the protons in the *endo* (**7** and **11**) but not in the *exo* (**6** and **8**) isomers.

(29) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **89**, 5485 (1967).

(30) Both the methoxymethine and the methoxy proton resonances of the diastereomer derived from (*R*)-O-methylmandelyl chloride and (+)-(*R*)-1-phenylethylamine are shifted upfield relative to the corresponding signals of the diastereomer derived from (*R*)-O-methylmandelyl chloride and (−)-(*S*)-1-phenylethylamine. The same behavior is exhibited by the analogous derivatives of 1-(1-naphthyl)ethylamine, in which the signals of the diastereomer derived[22c] from (*R*) acid chloride and (*R*) amine[31] are shifted upfield relative to those of the diastereomer derived from (*S*) acid chloride and (*R*) amine (and consequently to those of the diastereomer derived from (*R*) acid chloride and (*S*) amine).

(31) M. G. B. Drew, D. H. Templeton, A. Zalkin, J. Jacobus, and K. Mislow, unpublished work.

(32) (a) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1966); (c) M. Yamakawa and T. Kubota, *Shionogi Kenkyusho Nempo*, **15**, 109 (1965); *Chem. Abstr.*, **64**, 12053*b* (1966).

(33) D. J. Caldwell, Ph.D. Thesis, Princeton University, 1962; D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, **15**, 281 (1964); A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, **87**, 1813 (1965).

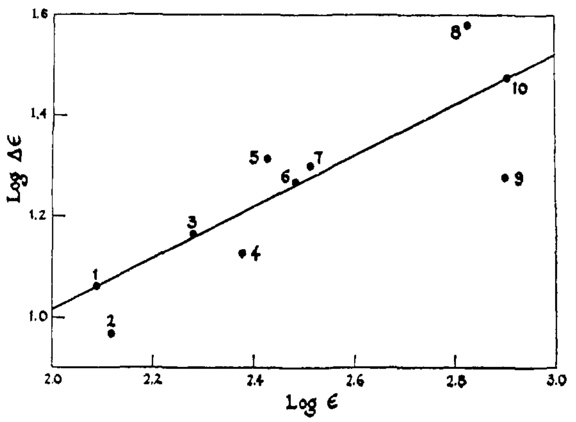

Figure 3. Linear plot (slope 0.5) of log $\Delta\epsilon$ *vs.* log ϵ of (+)-bicyclo-[2.2.2]oct-5-en-2-one (1), 1α-carbomethoxy-1β,5β-dimethyl-8α,-12α-etheno-13-oxo-*trans,anti,trans*-perhydrophenanthrene (2), (−)-4,4,5-trimethylbicyclo[3.2.0]hept-2-en-7-one (3), (+)-3,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (4), (−)-dehydronorcamphor (5), (−)-dehydrocamphor (6), (+)-dehydroepicamphor (7), (+)-dimethyldibenzsuberone (8), (+)-2-benznorbornenone (9), and parasantonide (10).

strength, in accord with experimental observation.[34] However, in view of the evident spectroscopic coupling between the carbonyl $n \rightarrow \pi^*$ and benzenoid $\pi \rightarrow \pi^*$ transitions in **1**, the above interpretation may have to be modified; it should be noted in this connection that the Cotton effect at 265 mμ is somewhat more intense than is usually observed for the lowest benzenoid $\pi \rightarrow \pi^*$ transition.[34]

The rotational strength of the $n \rightarrow \pi^*$ transition of (+)-**1** may be compared to that of other β,γ-unsaturated ketones by use of a relationship developed by Mason[6,35]

$$\log R = {}^1/_2 \log D + C \tag{1}$$

where R is the rotational strength of the optically active $n \rightarrow \pi^*$ transition, D the dipole strength of the same transition, and C a quantity whose invariance depends on the constancy of the angle subtended between the directions of the relevant electric and magnetic dipole transition moments.

Approximating R by $\Delta\epsilon$[36–38] and D by ϵ,[6,38,39] a plot of the pertinent experimental data[40] is given in Figure 3, where the slope has the theoretical value of 0.5. Considering the diversity in structural types of the β,γ-unsaturated ketones included, the fit of the experimental data to the Mason plot is remarkably good, and bears out the assumption that C is reasonably constant when the relative orientation of the carbonyl group and the double bond remains sensibly unchanged.[41]

Anomalies in the Asymmetric Hydroboration Reaction of Olefins. In the course of this work, the first example was encountered of an asymmetric hydroboration in which reaction of a given olefin with simple adducts of (+)-**4** and diborane gives rise to either enantiomer of the same substance, depending on the time elapsed before the reagents are mixed.[42,43] The reducing agent is the 1:1 adduct of (+)-**4** and $BH_3 \cdot THF$,[12] and the salient results of our study are collected in Table I.

Table I. Reactions of the 1:1 Adduct of $BH_3 \cdot THF$ and (+)-α-Pinene (**4**) with Benznorbornadiene (**2**)[a]

Run no.	Time delay, hr[b]	Reaction[c] temp, °C	$[\alpha]_D$, deg, of **5** in ethanol[d]
1	0	0	+5.1 (7.4)
2	21	0	−5.0 (7.2)
3[e]	0	25–28	+3.2 (4.6)
4	1	25–28	−3.8 (5.6)
5	21	25–28	−9.7 (14.0)
6	47	25–28	−9.7 (14.0)
7[f]	21	0	−4.9 (7.1)
8[g]	10.5	0	+2.8 (4.1)
9[g]	97	0	[h]

[a] A 2:1 molar ratio of (+)-**4**:**2** was employed. [b] The time elapsed after the reagent has formed and before the addition of **2**. In runs 1–7, the time delay is at 25–28°, while in runs 8–9, the time delay is at 0°. [c] Reaction time 3 hr. [d] *c* 4.9–6.4 g/100 ml. Optical purity of **5** given in parentheses. [e] The addition of **2** was carried out while the solution was being warmed to room temperature. [f] The solution was cooled to 0° and kept at that temperature for 3 hr before the addition of **2**. [g] Samples for these runs were removed from a stock solution. The ratio of (+)-**4**:**2** in these experiments is *ca.* 2:1. [h] α^{21}_D +0.01 ± 0.02° (*c* 5.4, *l* 2).

In all of this work, after the addition of (+)-**4** was completed, the solution was kept at 0° for 0.5 hr before the addition of **2** or warming to room temperature. It was found (see Experimental Section) that 96–97% of (+)-**4** had reacted in this period of time. As shown by runs 1 and 2, the time delay, defined as the time elapsed after the reagent had formed (*i.e.*, after the initial 0.5-hr period) and before **2** was added, crucially determined the stereochemical outcome of the reaction. As seen from the results of runs 3–6, no more than a 21-hr period of time delay is required to achieve a maximum of sign inversion; lesser periods may suffice.[44,45] This behavior appears not to be restricted to **2**: when *cis*-3-hexene was treated with the initial adduct of (+)-**4** and $BH_3 \cdot THF$ at 0° in THF (under conditions comparable to those of run 1 in Table I), the product

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(34) For a comprehensive survey of ORD and CD studies of aromatic compounds, see ref 7d.

(35) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

(36) R may equally well be approximated by the molecular amplitude (*a*) of the ORD curve.[6,35] A plot of log *a* *vs.* log ϵ for bicyclo[2.2.2]oct-5-en-2-one, dehydronorcamphor, and parasantonide has a slope of 0.5.[35]

(37) For dehydronorcamphor, the more recently found[10b] value of $\Delta\epsilon$ was employed. During the course of this work we also had occasion to remeasure the CD of (+)-dimethyldibenzsuberone in isooctane solution and found that the molecular ellipticity for the vibrational bands of the $n \rightarrow \pi^*$ transition at *ca.* 296.5 and 306.5 mμ is in somewhat better agreement with the theoretically calculated values[10a] than the previous measurement.[10a] Pertinent data are given in the Experimental Section.

(38) Values refer to the highest intensity in the vibrational envelope.

(39) For dimethyldibenzsuberone, the ϵ value is obtained after correction for overlap by the biphenyl conjugation band.[4]

(40) The data in Figure 3 are taken from the present work and from ref 5 and 10. We have excluded from this discussion compounds such as 3α-phenylcholestan-2-one[4,6,7a] and the arylbornenones,[5a] in which quantitative interpretation of the data is complicated by the conformational heterogeneity which results from torsion around the phenyl–carbon bond.

(41) There appears to be no need to fit the experimental data for β,γ-olefinic ketones with a line of slope other than 0.5.[5a]

(42) D. R. Boyd, M. F. Grundon, and W. R. Jackson [*Tetrahedron Lett.*, 2101 (1967)] have reported that asymmetric reduction of imines with lithium hydro-(1-butyl)bisisopinocampheylborate gives alkylpiperidines which are enantiomeric to those obtained by reduction with triisopinocampheyldiborane or **3**.

(43) H. C. Brown, N. R. Ayyangar, and G. Zweifel [*J. Amer. Chem. Soc.*, **86**, 1071 (1964)] have found that hydroboration of *cis*-2-butene with (−)-**3** gives (−)-2-butanol, whereas *trans*-2-butene gives (+)-2-butanol; the displacement of pinene in the latter reaction suggests that the hydroborating reagent in this case is triisopinocampheyldiborane.

(44) Under conditions comparable to those of run 5,[2] (−)-**5**, $[\alpha]_D$ − 8.9° (ethanol), was obtained by reaction of **2** in ether solution with a reagent generated by reaction of (+)-**4** with diborane.

(45) J. Katsuhara, H. Watanabe, K. Hashimoto, and M. Kobayashi [*Bull. Chem. Soc. Jap.*, **39**, 617 (1966)] report the use of a reagent whose composition might be comparable to that employed in runs 4–6.

was (−)-(*R*)-3-hexanol[46] (**12**), $[\alpha]^{24}\text{D}$ −1.47° (neat), 21% optically pure (based on the highest reported rotation[47]), whereas reaction with a solution of the hydroboration reagent kept at room temperature for 21 hr before use (as in run 5 in Table I) yielded (+)-(*S*)-**12**, $[\alpha]^{24}\text{D}$ +0.76° (neat), 11% optically pure. Although the sign inversion has thus been demonstrated for **2** and *cis*-3-hexene, it is not known to what extent this phenomenon is a general one.

To account for these observations it is suggested that the initial 1:1 adduct of (+)-**4** and $BH_3 \cdot THF$ undergoes rearrangement and/or disproportionation on standing at room temperature. This initial adduct is believed[12] to be 1,1-diisopinocampheyldiborane (**13**), predominating in equilibrium with (−)-**3** and $BH_3 \cdot THF$. If **13** rearranges to the *cis* and/or *trans*-1,2 isomer as the solution is warmed to room temperature,[48] the products of isomerization, acting as new asymmetric hydroborating species, are capable at least in principle of reversing the direction of the asymmetric synthesis, and this may account for the observed results. If such a rearrangement takes place, the possibility that it may be reversible on cooling to 0° must be considered. A comparison of entries 2 and 7 in the table suggests that this is not the case.

The role of **3** and triisopinocampheyldiborane (**14**) in the sign reversal was briefly investigated. Reaction of (−)-**3** with **2** under the conditions of run 5 gave **5**, $[\alpha]\text{D}$ +2.1° (ethanol), and a significant amount of unreacted **4**; this result was not surprising since **3** is dissociated at 0° in THF solution into **4** and **14**.[12] An attempt to allow **14** (prepared from (+)-**4**) to react with **2** under the conditions of run 5 afforded **5**, $[\alpha]\text{D}$ −5.7° (ethanol), and an appreciable amount of unreacted **4**. Since the rotation of (−)-**5** in this case is somewhat lower than that of entry 5, and since pinene is displaced in the reaction, this result *suggests* that **14** does not play a dominant role in the sign reversal.

Granted, as suggested above, that rearrangement of **13** to 1,2-diisopinocampheyldiborane may account for the change in stereochemistry, unanswered questions remain concerning the relative amounts of **13** and of the 1,2 isomer, the ratio of the *cis*- and *trans*-1,2 isomers, and the preferred conformations of any of these substances. Under these circumstances, a detailed mechanistic interpretation of our results, such as that proposed[14] for the asymmetric hydroborations of olefins by **3**, does not seem warranted at this time.

Experimental Section[49]

Benznorbornadiene (2). This material was prepared by the method of Wittig and Knauss[32a] or, alternatively, from benzenediazoniumcarboxylate hydrochloride and cyclopentadiene, according to the procedure of Friedman and Logullo.[50] The samples of **2** used in this work had $n^{20}\text{D}$ 1.5656–1.5664 (lit.[32a] $n^{20}\text{D}$ 1.5654–1.5668).

(+)-α-Pinene (4). The sample used, which was that described previously,[9] had $[\alpha]^{25}\text{D}$ +38.3° (neat), $[\alpha]^{23.5}\text{D}$ +42.5° (*c* 2.1, ethanol) (lit.[9] $[\alpha]^{22.5}\text{D}$ +43° (*c* 2.0, ethanol)), $n^{21}\text{D}$ 1.4657 (lit.[13] $n^{20}\text{D}$ 1.4660), and was *ca.* 75% optically pure based on the highest reported rotation, $[\alpha]^{20}\text{D}$ +51.1° (neat).[51]

(+)-*exo*-2-Benznorbornenyl Acetate (5). Boron trifluoride etherate (4.54 g, 32 mmol) was added to a solution of (+)-**4** (8.71 g, 64 mmol) and sodium borohydride (0.91 g, 24 mmol) in 20 ml of diglyme at 0° under nitrogen. The resulting suspension was stirred for 3 hr at 0°. A solution of **2** (4.55 g, 32 mmol) in 10 ml of diglyme was added, and stirring was continued for an additional 3 hr at 0°. The reaction mixture was oxidized with 3 *N* sodium hydroxide (13 ml) and 30% hydrogen peroxide (15 ml) at 30–50°. The crude product was extracted with ether, the ether extracts were washed with 2% sodium sulfite solution and water, and the organic layer was dried over anhydrous magnesium sulfate. Evaporation of the ether gave an oil which was acetylated by stirring overnight at room temperature with a mixture of acetic anhydride (18 ml) and pyridine (15 ml). This solution was poured into water and extracted with ether. The ether layer was washed with saturated sodium bicarbonate (until evolution of carbon dioxide had ceased) and water and was dried over magnesium sulfate. The crude acetates were fractionated under reduced pressure to remove most of the isopinocampheyl acetate (bp 85–98° (5 mm)). The distillation residue was chromatographed on silica gel (80–200 mesh) in 50:50 hexane–benzene and **5** was eluted with benzene. The product was further purified by distillation (kugelrohr, 85–95°, 0.25 mm) to give a colorless liquid, $[\alpha]^{25}\text{D}$ +31.7° (*c* 6.0, ethanol), which was identified as **5** by its nmr spectrum which is in satisfactory agreement with that reported,[52] and by its infrared spectrum (C=O stretch at 1740 cm^{-1}). Glpc analysis on a 6-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 184°, helium flow rate 30 cc/min, indicated the presence of *ca.* 1% of *endo*-2-benznorbornenyl acetate (see below), retention time 10.3 min, with **5** at retention time 12.0 min.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.19; H, 6.98. Found: C, 77.51; H, 6.93.

When a solution of (−)-**3**, from $BH_3 \cdot THF$ (45 mmol) and (+)-**4** (1.32 g, 9.7 mmol) was allowed to react with **2** (0.62 g, 4.4 mmol) *in THF* at 0° under conditions analogous to that described above for this reaction in diglyme, the product, **5** (0.32 g, 36% yield), had $[\alpha]^{24}\text{D}$ +17.9° (*c* 5.5, ethanol).

In an additional experiment, $BH_3 \cdot THF$ (4.5 mmol) and (+)-**4** (1.21 g, 8.9 mmol) were allowed to react at 0° for 0.5 hr, the solution was stirred for *21 hr at room temperature*, **2** (0.63 g, 4.4 mmol) was added, and the solution was stirred for an additional 3 hr at room temperature. Hydrolysis (see below) indicated 0.74 mmol of unreacted hydride and glpc analysis indicated 1.6 mmol of unreacted **4**. The product, **5** (0.46 g, 51% yield), had $[\alpha]^{21}\text{D}$ +2.8° (*c* 5.3, ethanol). In a separate experiment, $BH_3 \cdot THF$ (4.9 mmol) and (+)-**4** (2.70 g, 19.8 mmol) were allowed to react with **2** (1.40 g, 9.9 mmol) as above. Hydrolysis indicated 3.3 mmol of unreacted hydride, and glpc analysis indicated 5.2 mmol of unreacted **4** and 1.1 mmol of unreacted **2**. The product, **5** (1.14 g, 64% yield), had $[\alpha]^{24}\text{D}$ +2.1° (*c* 5.3, ethanol).

(+)-*exo*-2-Benznorbornenol (6). A solution of (+)-**5** (2.9 g, 14.4 mmol), $[\alpha]^{25}\text{D}$ +31.7° (*c* 6.0, ethanol), in ether was added to lithium aluminum hydride (0.57 g, 15 mmol) in ether, and the mixture was refluxed for 4 hr. The complex was decomposed with 3 *N* NaOH. Extraction with ether, drying over magnesium sulfate, and evaporation gave a quantitative yield of the crude product. This material was chromatographed on silica gel, and **6**, eluted with 75:25 v/v benzene–ether, was further purified by distillation (kugelrohr, 75–85°, 0.1 mm) to give a white solid, mp 54.5–69° (lit. mp for racemic material 74.1–75.4°,[18] 74.5–75.5°[53]), $[\alpha]^{26}\text{D}$ +15.8° (*c* 4.2, chloroform). The infrared spectrum of (+)-**6** was in satisfactory agreement with that reported[18,54] for racemic **6**, and its nmr spectrum (aromatic multiplet at τ 2.75–3.2 (4 H), *endo* C-2 proton, broad, at τ 6.13, bridgehead protons at τ 6.60–6.95, OH proton at τ 7.58, methylene multiplet at τ 7.75–8.45 (4 H)

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(46) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **76**, 415 (1928).

(47) R. S. Airs, M. P. Balfe, and J. Kenyon, *J. Chem. Soc.*, 18 (1942).

(48) A time-dependent rearrangement of a 1,1-dialkyldiborane to a 1,2-dialkyldiborane has been observed by B. M. Mikhailov and L. S. Vasil'ev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 580 (1962).

(49) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Nmr spectra were measured on a Varian A-60A spectrometer in *ca.* 10% carbon tetrachloride solution using tetramethylsilane as internal standard, unless otherwise specified. Ultraviolet absorption spectra were measured on a Cary 14 recording spectrophotometer. Optical rotatory dispersion and circular dichroism were measured on a Cary 60 recording spectropolarimeter and a Cary Model 6001 circular dichroism accessory, respectively.

(50) L. Friedman, private communication. We thank Professor Friedman for providing us with details of this procedure prior to publication.

(51) F. H. Thurber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931).

(52) S. J. Cristol and R. Caple, *J. Org. Chem.*, 31, 2741 (1966).

(53) P. Bruck, *Tetrahedron Lett.*, 449 (1962).

(54) W. P. Giddings, Ph.D. Thesis, Harvard University, 1959.

(lit.[52] *endo* C-2 proton at τ 6.17)) is in accord with the structure. Addition of D_2O to the nmr tube causes immediate disappearance of the OH signal.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.45; H, 7.56. Found: C, 82.58; H, 7.72.

(+)-2-Benznorbornenone (1). A mixture of (+)-**6** (2.18 g, 13.6 mmol), $[\alpha]^{26}_{\mathrm{D}}$ +15.8° (*c* 4.2, chloroform), benzoquinone (1.70 g, 15.7 mmol), and aluminum *t*-butoxide (6.58 g, 26.7 mmol) in 170 ml of benzene was refluxed for 48 hr, following the procedure of Bartlett and Giddings.[18] After chromatography of the crude product on alumina, (+)-**1** was obtained by distillation (kugelrohr, 65–75°, 0.02 mm), $[\alpha]^{25}_{\mathrm{D}}$ +262° (*c* 1.8, isooctane).

The material was $\geq 99\%$ pure by glpc analysis on a 6-ft silicone rubber SE-30 column (described above) at 179°, helium flow rate 30 cc/min, retention time 7.7 min. The infrared spectrum was in satisfactory agreement with that reported.[18] The nmr spectrum featured the following resonances: aromatic multiplet at τ 2.72–3.12 (4 H), bridgehead protons (multiplet) at τ 6.35–6.68 (2 H), methylene multiplet at τ 7.45–8.45 (4 H). The ultraviolet absorption spectrum in isooctane solution exhibited the following features: $\lambda_{\max}$ mμ (ϵ) 321 (524), 308.8 (796), 298 (702), 288.5 (487), 274 (624), 266 (584), 232 (3670), 226.5 (5740), 221 (5740), 199 (30,000) (lit.[55] for racemic **1**: 321 (501), 308 (795), 297.5 (708), 288 (490), 273.5 (616), 266 (589)). The ORD characteristics in isooctane (*c* 0.0588 g/100 ml at $\lambda > 230$ mμ, *c* 0.00372 at $\lambda \leq 230$ mμ, a sample of (+)-**1**, $[\alpha]^{24}_{\mathrm{D}}$ +221° (*c* 0.40, isooctane), was used at $\lambda < 230$ mμ), corrected to optical purity, were $[\phi]_{322.5}$ +42,800°, $[\phi]_{318}$ +14,400°, $[\phi]_{311}$ +25,900°, $[\phi]_{307.5}$ 0°, $[\phi]_{304}$ −10,500°, $[\phi]_{299}$ −9400°, $[\phi]_{294}$ −29,500°, $[\phi]_{288}$ −30,000°, $[\phi]_{276}$ −41,100°, $[\phi]_{204}$ −75,000°, $[\phi]_{198}$ 0°. The CD in isooctane, corrected to optical purity (*c* 0.0606 g/100 ml at $\lambda > 230$ mμ, *c* 0.00606 at $\lambda < 230$ mμ), was as follows: $\lambda_{\max}$ mμ ($[\theta] \times 10^{-4}$) 340 (0), 319 (+4.3), 307.5 (+6.2), 296 (+4.9), 286 (+2.8), 274 (0), 272 (−0.45), 265 (−0.72), 245 (0), 232.5 (+0.4), 230 (0); $[\theta] < 0$ below 225 mμ.

Anal. Calcd for $C_{11}H_{10}O$: C, 83.50; H, 6.37. Found: C, 83.63; H, 6.34.

Racemic *endo*-2-Benznorbornenol (7). This material was prepared as described by Bartlett and Giddings.[18] The crude product, which contained small amounts of **6**, was either crystallized twice from petroleum ether (bp 30–60) and sublimed (50–60°, 0.2 mm) to give a solid, mp 72.5–75° (lit.[18] mp 74.5–75.4°), or distilled (kugelrohr, 80°, 0.05 mm) to give a white solid, mp 69–72°, which was shown by glpc analysis on a 2-ft column of 10% Carbowax 20M on 60–80 mesh Chromosorb W at 170°, helium flow rate 60 cc/min, to contain *ca.* 5% of **6**; the retention times of **7** and **6** were 5.7 and 10.0 min, respectively. The nmr spectrum showed the following resonances: aromatic multiplet at τ 2.64–3.20 (4 H), broad multiplet at τ 5.38–5.93 (*exo* C-2 proton), bridgehead protons as a broadened signal at τ 6.65–6.99, multiplet at τ 7.52–8.62 (3 H), and multiplet at τ 8.86–9.57 (2 H). Addition of D_2O (two drops) to the nmr tube slowly resulted in partial disappearance of the downfield portion of the τ 8.86–9.57 resonances, and added fine structure to the *exo* C-2 proton resonance. The relative rates of disappearance of the OH proton in **7** and **6** (see above) are noteworthy. The remainder of the resonance at τ 8.86–9.57 is assigned to the *endo* C-3 proton, by analogy to the reported spectra of *endo*-dehydronorbornyl derivatives.[56]

Racemic *endo*-2-Benznorbornenyl Acetate. Racemic **7** (ratio **7**:**6** *ca.* 94:6, 0.16 g, 1.0 mmol) was mixed with 1 ml each of acetic anhydride and pyridine and allowed to stand overnight at room temperature. The product was isolated as described above for **5** and purified by distillation (kugelrohr, 65–70°, 0.02 mm) to give a colorless liquid, 0.14 g (69%), *endo–exo* ratio *ca.* 92:8 by glpc analysis. The nmr spectrum had the following features: aromatic multiplet at τ 2.65–3.25 (4 H), *exo* C-2 proton multiplet at τ 4.55–4.9, multiplets at τ 6.25–6.45 and 6.65–6.85 for the bridgehead protons, multiplet at τ 7.45–8.5 (3 H), methyl singlet at τ 8.3 (3 H), and *endo* C-3 proton[56b] multiplet at τ 8.75–9.15. A benzene solution of **5** to which had been added 1% of the *endo* acetate prepared above was analyzed by glpc on the 6-ft silicone rubber column described above at 192°, helium flow rate 30 cc/min. The *endo* acetate appeared as a shoulder at retention time 6.0 min (peak height 1) and **5** appeared at retention time 7.0 min (peak height 80). It is thus apparent that as little as 1% of *endo*-2-benznorbornenyl acetate is detectable in **5** under these conditions.

(+)-*endo*-2-Benznorbornenol (7). This material was prepared by the procedure described for the racemic compound. A solution of (+)-**1** (0.23 g, 1.46 mmol), $[\alpha]^{25}_{\mathrm{D}}$ +262° (*c* 1.82, isooctane), was allowed to react with lithium aluminum hydride (0.07 g, 1.84 mmol). The product was purified by distillation (kugelrohr, 70–80°, 0.07 mm) to give 0.16 g (69%) of a white solid, mp 68–90°, $[\alpha]^{22}_{\mathrm{D}}$ +39.1° (*c* 4.0, chloroform). Glpc analysis (as above for racemic **7**) indicated the presence of *ca.* 2% of **6**.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.45; H, 7.56. Found: C, 82.24; H, 8.02.

***exo*-2-Benznorbornenyl O-Methylmandelate.** A solution of pyridine (0.98 g, 12.4 mmol) and of (+)-**6** (0.16 g, 1.0 mmol), $[\alpha]^{26}_{\mathrm{D}}$ +0.7° (*c* 4.7, chloroform), in benzene was added to a benzene solution of racemic O-methylmandelyl chloride, prepared[22c] from O-methylmandelic acid (1.2 mmol), at room temperature with stirring over a period of 15 min. The work-up was carried out as described for the O-methylmandelamides.[22c] The crude product was chromatographed on Florisil, and the desired product was eluted with benzene and 90:10 v/v benzene–ether. The nmr spectrum (benzene solution[57]) of the chromatographed material featured a single methoxymethine proton signal at 148 Hz and a single methoxy proton signal at 237 Hz. An analytical sample was obtained as a viscous oil by distillation (kugelrohr, 120–150°, 0.03 mm).

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.88; H, 6.54. Found: C, 78.49; H, 6.44.

***endo*-2-Benznorbornenyl O-Methylmandelate.** Optically pure O-methylmandelyl chloride, prepared[22c] from (−)-O-methylmandelic acid (0.62 mmol), was allowed to react with pyridine (0.16 g, 2.0 mmol) and racemic **7** (0.042 g, 0.26 mmol) in benzene, as previously described[10b] for the dehydronorbornyl analog. The product obtained after work-up was sufficiently pure for examination by nmr spectroscopy, and the nmr spectrum in benzene solution featured the following signals.[57] The methoxymethine protons in the mixture of diastereomers derived from **7** appeared at 161 and 167 Hz, while the methoxy protons appeared at 242 and 247 Hz. Electronic integration of the methoxymethine and methoxy resonances for the diastereomers derived from **7** indicated a ratio of 1:1.

Determination of the Optical Purity of (+)-*endo*-2-Benznorbornenol (7). Optically pure O-methylmandelyl chloride, prepared from (−)-O-methylmandelic acid (0.71 mmol), was allowed to react with pyridine (0.16 g, 2.0 mmol) and (+)-**7** (0.046 g, 0.29 mmol), $[\alpha]^{22}_{\mathrm{D}}$ +39.1° (*c* 4.0, chloroform), as above, for 17 hr at room temperature. Since impurities were indicated in the nmr spectrum of the crude ester, the product was chromatographed on Florisil and eluted with 1:1 and 2:1 v/v benzene–hexane. Integration of the methoxymethine and of the methoxy resonances in benzene solution indicated that the ratio of diastereomers in the O-methylmandelate derived from (+)-**7**, and hence the ratio of enantiomers in (+)-**1**, was 2.7:1.0. The signals at 167 and 247 Hz are more intense than those at 161 and 242 Hz, respectively. The sample used for the nmr spectra was distilled (kugelrohr, 130–150°, 0.075 mm) to give an off-white solid.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.88, H, 6.54. Found: C, 77.58; H, 6.58.

Asymmetric Synthesis of Methyl *p*-Tolyl Sulfoxide (9) Induced by (+)-*exo*-Benznorbornenol (6). *p*-Toluenesulfinyl chloride[58] (0.28 g, 1.6 mmol) was stirred at −78° in ether solution under nitrogen. A solution of (+)-**6** (0.25 g, 1.6 mmol), $[\alpha]^{25}_{\mathrm{D}}$ +5.8° (*c* 4.6, chloroform), and pyridine (0.98 g, 12.4 mmol) in ether was added over a period of 15 min; a precipitate (pyridine hydrochloride) appeared immediately. Stirring was continued for 0.5 hr at −78°, and the solution was warmed to room temperature. The precipitate was filtered, and the ether solution was washed consecutively with 1% hydrochloric acid and water, dried over magnesium sulfate, and evaporated to give an oil which was dissolved in ether and allowed to react with an excess of methylmagnesium iodide. The excess Grignard reagent was decomposed with saturated ammonium chloride solution, and the products were taken up in ether. The ether was extracted five times with 100-ml portions of water. The combined aqueous extracts were saturated with sodium chloride and the salt solution was extracted three times with 150-ml

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[55] K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 84, 1455 (1962).

[56] (a) P. Laszlo and P. von R. Schleyer, *ibid.*, 86, 1171 (1964); (b) J. Paasivirta, *Suomen Kemistilehti, B*, 38, 130 (1965).

[57] Chemical shifts in benzene solution are reported in hertz upfield from internal benzene.

[58] F. Kurzer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 937.

portions of chloroform. The combined chloroform extracts were dried over magnesium sulfate and evaporated to give an oil which was chromatographed on silica gel in benzene. The product, **9**, was eluted with ethyl acetate and further purified by distillation (kugelrohr, 65–75°, 0.03 mm) to give 0.07 g of a white solid (28.5%). Glpc analysis of this material on a 2-ft column of 10% Carbowax 20M (described above) at 171°, helium flow rate 60 cc/min, indicated homogeneity, retention time 13.2 min. The ORD characteristics in ethanol (*c* 0.63) were $[\phi]_{400}$ +11.4°, $[\phi]_{370}$ +17.3°, $[\phi]_{350}$ +22.6°, $[\phi]_{320}$ +39.2°, $[\phi]_{300}$ +67.8°. The ORD characteristics in ethanol of optically pure (+)-**9**[59] (*c* 0.05) were $[\phi]_{400}$ + 800°, $[\phi]_{370}$ +1170°, $[\phi]_{350}$ +1540°, $[\phi]_{320}$ +2630°, $[\phi]_{300}$ +4560°. The sample of (+)-**9** obtained in the present experiment is therefore 1.5% optically pure.

(+)-*exo*-Dehydronorborneol (8). The present procedure for the preparation of **8** was worked out as an alternative to that previously described.[9] A heterogeneous mixture of (+)-*exo*-bicyclo[2.2.1]-hept-5-en-2-yl acetate[9,60] (3.5 g, 23 mmol), $\alpha^{22}\mathrm{D}$ +23.45° (*l* 1, neat), $n^{25}\mathrm{D}$ 1.4652, and anhydrous potassium carbonate (3.4 g, 24.6 mmol) was refluxed in methanol (150 ml) for 3.5 hr. A portion of the solvent was distilled, the distilled solvent and methyl acetate were replaced with fresh methanol, and refluxing was continued for 4 hr, when the distillation–methanol replacement process was repeated. The solvent was distilled, and the residue was taken up in carbon tetrachloride. The carbon tetrachloride solution was washed with water, and the aqueous extracts were washed with carbon tetrachloride and chloroform. The combined organic extracts were washed with water and dried over magnesium sulfate, and the solvent was removed. The dark brown residue was distilled (kugelrohr, 50–70°, 1 mm) to give a white solid (1.59 g, 64% yield). Since glpc analysis indicated that this material contained *ca.* 5% of impurities, it was recrystallized from petroleum ether (bp 30–60°). Glpc analysis of the crystallized material showed no increase in purity. The filtrate was distilled (kugelrohr, 45–65°, 0.1 mm) to give 0.95 g of **8**, mp 85–91.5° (lit.[9] mp 86–92°), $[\alpha]^{25}\mathrm{D}$ +6.8° (*c* 8.8, chloroform). Glpc analysis of this material on a 6-ft column of 10% Carbowax 4000 on 60–80 mesh Chromosorb W at 138°, helium flow rate 30 cc/min, showed impurities totalling less than 3% at retention times 4.9, 14.8, and 16.8 min, with **8** (>97% pure) at retention time 21.6 min.

Asymmetric Synthesis of Methyl *p*-Tolyl Sulfoxide (9) Induced by (+)-*exo*-Dehydronorbornenol (8). *p*-Toluenesulfinyl chloride (0.57 g, 3.3 mmol) was allowed to react with (+)-**8** (0.36 g, 3.3 mmol), $[\alpha]^{25}\mathrm{D}$ +6.8° (*c* 8.8, chloroform), and pyridine (0.80 g, 10 mmol) at −78°, as described above. Reaction with methylmagnesium iodide and subsequent work-up were analogous. The crude product (0.25 g) was chromatographed to give **9**, which was shown by glpc analysis, as above, to contain small amounts of unidentified impurities at retention times 1.4, 1.9, 5.0, and 6.6 min, with **9** >97% pure. The ORD characteristics in ethanol (*c* 2.63) were $[\phi]_{400}$ +21.5°, $[\phi]_{370}$ +30.8°, $[\phi]_{350}$ +41.4°, $[\phi]_{320}$ +72.3°, $[\phi]_{300}$ +124.8°. This sample of **9** is therefore 2.7% optically pure.

Reactions of the 1:1 Adduct of $BH_3\cdot THF$ and (+)-α-Pinene (4) in Tetrahydrofuran Solution and Related Experiments. General Procedures. The concentration of the $BH_3\cdot THF$ solution was determined either by active hydride analysis[61] or by reaction of the $BH_3\cdot THF$ with acetone, hydrolysis,[61] and titration of the boric acid formed with mannitol.[62] Independent comparison of the two methods gave results which were in satisfactory agreement. The glassware used was baked dry in an oven at 100° overnight and assembled under nitrogen. After $BH_3\cdot THF$ was introduced at 0°, the apparatus was closed and the other reagents were introduced through a serum cap, *via* syringe. Unreacted hydride was measured by displacement of water[63] by the hydrogen liberated after hydrolysis of the reaction mixture, which was oxidized with alkaline peroxide and worked up as described above for the preparation of **5**. The ether solution was analyzed for unreacted **4** by glpc analysis on the 6-ft 10% silicone rubber column described above, at 160°, helium flow rate 30 cc/min; the retention time of **4** was 2.0 min. Unless otherwise specified, only trace amounts of **4** (<2.5% of the initial amount) were detected. In reactions involving **2**, the crude alcohols were acetylated and worked up, as described above. Isopinocampheyl acetate and **5** were separated by preparative glpc on the 20 ft × 3/8 in. 30% silicone rubber SE-30 column described above at 210°, helium flow rate 200 cc/min; retention times of isopinocampheyl acetate and **5** were 12–17 and 24–36 min, respectively. The **5** thus obtained was further purified by distillation (kugelrohr). It was identified by its ir spectrum and was then homogeneous by glpc analysis and ir.

Formation of the 1:1 Adduct of $BH_3\cdot THF$ and (+)-α-Pinene (4) at 0°. BH_3.THF (5.6 mmol) and (+)-**4** (0.76 g, 5.6 mmol) were allowed to react at 0° for 0.5 hr. Glpc analysis indicated that 0.15 mmol (2.6%) of **4** was unreacted. Isopinocampheol (0.65 g, 75%) was recovered. It is apparent that $BH_3\cdot THF$ and (+)-**4** react to the extent of 96–97% under these conditions.

Reactions of the 1:1 Adduct of BH_3.THF and (+)-α-Pinene (4) with Benznorbornadiene (2). Under a Variety of Conditions. The reaction conditions and results are exemplified by those in run 1 as follows. $BH_3\cdot THF$ (10.1 mmol) and (+)-**4** (1.36 g, 10.1 mmol) were allowed to react at 0° for 0.5 hr, and **2** (0.72 g, 5.1 mmol) was added. The solution stirred for 3 hr at 0°. Hydrolysis with water indicated the presence of 14.6 mmol of unreacted hydride. The product, **5** (0.55 g, 54%), had $[\alpha]^{27}\mathrm{D}$ +5.1° (*c* 5.3, ethanol). The reaction conditions and results of runs 1–9 are collected in Tables I and II.

Table II. Reactions of the 1:1 Adduct of $BH_3\cdot THF$ and (+)-α-Pinene (**4**) with Benznorbornadiene (**2**)

Run no.[a]	$BH_3\cdot$ THF[b,c]	(+)-**4**[b]	**2**[b]	Unreacted hydride[b]	**5**, % yield
1	10.1	10.1	5.0	14.6	54
2	10.4	10.4	5.2	12.2	55
3	9.9	9.9	5.0	15.0	60
4	10.1	10.0	5.0	14.2	64
5	10.1	10.0	5.0	14.2	69
6	4.4	4.4	2.2	5.3	53
7	5.1	5.1	2.5	5.3	25
8	. . .	. . .	4.1	9.6	54
9	. . .	. . .	4.0	5.8	46

[a] Run numbers correspond to those in Table I. [b] In millimoles. [c] The solution was *ca.* 1.1 *M* in BH_3.

Reaction of Triisopinocampheyldiborane (14) with Benznorbornadiene (2) in Tetrahydrofuran at Room Temperature. A solution of **14**, prepared from $BH_3\cdot THF$ (4.5 mmol) and (+)-**4** (0.92 g, 6.7 mmol) at 0° for 0.5 hr, was kept at room temperature for 21 hr, **2** (0.48 g, 3.4 mmol) was added, and the reaction mixture was kept at room temperature for 3 hr. Hydrolysis indicated 2.9 mmol of unreacted hydride, and glpc analysis indicated 1.0 mmol of unreacted **4**. The product, **5** (0.35 g, 52% yield), had $[\alpha]^{21}\mathrm{D}$ −5.7° (*c* 5.4, ethanol).

Asymmetric Hydroboration of Benznorbornadiene (2) in Ether. Diborane (generated from sodium borohydride (30 mmol) and boron trifluoride etherate (11.1 g, 78 mmol) in the apparatus described by Zweifel and Brown[64]) was led into a solution of (+)-**4** (5.44 g, 40 mmol) at 0° under nitrogen. After the addition of diborane was complete, the solution stirred overnight at room temperature. A solution of **2** (2.82 g, 20 mmol) in ether was added, and the mixture was stirred for 3 hr at room temperature. About half of the solution was worked up as usual to give **5** (1.4 g), $[\alpha]^{24.5}\mathrm{D}$ −8.9° (*c* 5.2, ethanol). The remainder of the solution was worked up 24.5 hr after the addition of **2** to give **5** (1.0 g), $[\alpha]^{25}\mathrm{D}$ −8.5° (*c* 5.5, ethanol).

Reactions of the 1:1 Adduct of $BH_3\cdot THF$ and (+)-α-Pinene (4) with *cis*-3-Hexene. $BH_3\cdot THF$ (56 mmol) and **4** (7.62 g, 56 mmol) were allowed to react at 0° for 0.5 hr. *cis*-3-Hexene (2.35 g, 28 mmol), bp 65–67°, $n^{20}\mathrm{D}$ 1.3955 (lit.[65] bp 67.1°, $n^{20}\mathrm{D}$ 1.3957),[66] was

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(59) Dr. P. Laur, unpublished observation.

(60) The crude acetate may be conveniently purified by preparative glpc on a 20 ft × 3/8 in. column of 30% silicone rubber SE-30 on 45–60 mesh Chromosorb W at 170°, helium flow rate 200 cc/min. Under these conditions, the product had a retention time of 12.4 min. An unidentified impurity (<2%) was observed at retention time 14.9 min.

(61) R. D. Strahm, "Treatise on Analytical Chemistry," Part II, Section B, Vol. 12, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 169 ff.

(62) G. Fowles, "Volumetric Analysis," G. Bell and Sons, Ltd., London, 1932, p 182.

(63) P. W. Mullen, "Treatise on Analytical Chemistry," Part I, Vol. 7, I. M. Kolthoff, P. J. Elving, and E. B. Sandell, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 4317 ff.

(64) G. Zweifel and H. C. Brown, "Organic Reactions," Vol. 13, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 31–32.

(65) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **81**, 1512 (1959).

(66) The material, prepared from 3-hexyne as described,[65] contains about 1% of the starting material by glpc (silicone rubber column at 60°).

added, and the solution was stirred at 0° for 3 hr. Alkaline peroxide oxidation, work-up in the usual manner, distillation of the solvent, and distillation of the residue at temperatures up to 140° gave crude 3-hexanol (**12**) contaminated by traces of **4**. Chromatography on alumina (80–200 mesh) in pentane, elution with ether, and distillation (kugelrohr, 125–140°) of the eluate gave 0.90 g (32% yield) of **12**, $n^{20}\mathrm{D}$ 1.4158, $[\alpha]^{24}\mathrm{D}$ −1.47° (neat) (lit. $n^{20}\mathrm{D}$ 1.4167,[67] $[\alpha]^{20}\mathrm{D}$ +7.09° (neat)[47]). Glpc analysis (6-ft 10% column of Carbowax 4000, at 130°, helium flow rate 30 cc/min) indicated the presence of 3-hexanone (*ca.* 3%), of an unidentified impurity (*ca.* 2%), and of **12**, with retention times of 2.8, 3.6, and 4.4 min, respectively.

In a separate experiment, $BH_3 \cdot THF$ (56 mmol) and (+)-**4** (7.62 g, 56 mmol) were allowed to react at 0° for 0.5 hr and the solution was then kept at room temperature for 21 hr. *cis*-3-Hexene (2.352 g, 28 mmol) was added and the solution stirred at room temperature for 3 hr. Work-up and purification, as above, gave 0.70 g (24.5% yield) of **12**, $n^{20}\mathrm{D}$ 1.4162, $[\alpha]^{24}\mathrm{D}$ +0.76° (neat). Glpc analysis, as above, indicated that **12** was contaminated with *ca.* 1% each of 3-hexanone and the unidentified contaminant.

Circular Dichroism of (+)-Dimethyldibenzsuberone. The sample used had the following properties: $[\alpha]\mathrm{D}$ +617.7° (*c* 1.4, benzene), uv in isooctane solution λ_{max} mμ (ϵ) 317 (263), 307 (584), 297.5 (752), 289 (746); CD in isooctane solution (*c* 0.0464 g/100 ml at $\lambda >$ 260 mμ, *c* 0.00464 g/100 ml at $\lambda <$260 mμ) λ_{max} ([θ]) 335 (0), 316 (+5.5 × 10^4), 306.5 (+11.2 × 10^4), 296.5 (+12.5 × 10^4), 289.5 (+9.3 × 10^4), 280 sh (+4.3 × 10^4), 245 (10 × 10^4) [lit. $[\alpha]^{23}\mathrm{D}$ +617° (*c* 1.65, benzene);[55] uv[55] 317 (257), 307 (575), 297.5 (759), 289.5 (759); CD[10a] 296 (+10.8 × 10^4), 245 (+9.65 × 10^4).

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[67] R. Lespieau and R. Lombard, *Bull. Soc. Chim. Fr.*, **2**, 369 (1935).

Stereochemistry of 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene[1,2]

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Abstract: In an asymmetric transfer reaction, two optically active diastereomers of 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene (**1**) are formed by Stevens rearrangement of an optically active bridged biphenyl azepinium bromide (**2**). The isomers, which differ in the chirality of the biphenyl moiety but share the same chirality at the asymmetric carbon atom (C-9), interconvert by torsion around the biphenyl pivot bond axis, and are isolated in crystalline forms which arise by second-order asymmetric transformations. First-order rate constants of mutarotation, the equilibrium constant between the isomers, and the Arrhenius and the transition-state parameters for the interconversion have been determined. From an analysis of the optical rotatory dispersion and nmr spectra of the products of rearrangement of (+)-(*S*)-**2**, the *S* configuration has been assigned to C-9 in both diastereomers and the *R* and *S* configurations to the biphenyl moieties in (−)-**1** and (+)-**1**, respectively. These results are in consonance with current views on the mechanism of the Stevens rearrangement. In connection with the configurational and conformational analysis, a brief discussion is offered on the limitations and applicability of the Wood–Fickett–Kirkwood method for determining thermodynamic parameters from the temperature dependence of physical properties.

Optically active 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene (**1**) is obtained as a basic oil when optically active 1,1,4′,1′′-tetramethyl-2,7-dihydro-3,4,5,6-dibenzazepinium bromide (**2**) is treated with phenyllithium in ether.[3] This reaction involves an asymmetric transfer, in which an asymmetric carbon atom (at C-9 of **1**) is generated in a Stevens rearrangement[4] from a compound having only biphenyl chirality.[5] In our hands, the rearrangement of (+)-**2** yielded **1** which eventually crystallized; the material thus obtained was dextrorotatory, (+)-**1**. Subsequent crystallizations of the *same* basic oil yielded the levorotatory form, (−)-**1**. Evidently the two crystalline forms (+)-**1** and (−)-**1** arise by second-order asymmetric transformations,[6] the separation of the crystalline phase displacing the equilibrium between the two diastereomers in the supernatant solution. As will be discussed in further detail below, both (+)-**1** and (−)-**1** were found to mutarotate in toluene to give the same equilibrium mixture, whose sign of rotation was found to be temperature dependent; the rate of mutarotation was found to follow strict first-order kinetics.

Reaction of (+)-**2** with potassium amide in liquid ammonia gave as the major products 4,5-dimethylphenanthrene (**3**) and 9,10-dihydro-4,5-dimethylphenanthrene (**4**), the ratio of **3**:**4** decreasing with increasing reaction time. For example, the ratio of **3**:**4** was 0.012 after 1-hr reaction time, and 17.6 after 1 week. After a reaction time of 8 months, only **4** could be observed. With weaker bases, such as potassium hydroxide in liquid ammonia, **1** was produced. It thus appears that when the reactant is potassium hydroxide, the reaction stops largely at the rearrangement stage, whereas reaction with potassium amide removes a benzylic hydrogen from C-10 of the

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[2] For a preliminary account of portions of this work, see K. Mislow and H. Joshua, *J. Amer. Chem. Soc.*, **87**, 666 (1965).

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[4] Transfer of asymmetry from nitrogen to carbon in a Stevens rearrangement has recently been described by R. K. Hill and T. Chan, *J. Amer. Chem. Soc.*, **88**, 866 (1966).

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[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 42 ff.