2.58–2.52 (m, 2), 2.44–2.38 (m, 2), 2.16 (t, J = 7.4 Hz, 2), 2.06 (s, 3), 1.48–1.25 (m, 6), 0.87 (t, J = 6.9 Hz, 3); ^{13}C NMR 209.04, 169.47, 140.41, 34.26, 31.75, 31.44, 28.03, 22.95, 22.47, 17.17, 13.99.

Acknowledgment. This work was supported, in part, by the Ministero della Pubblica Istruzione, Roma.

Registry No. **4**, 113810-80-3; **6a**, 60721-34-8; **6b**, 32776-14-0; **6c**, 113810-81-4; **6d**, 113810-82-5; **6e**, 7018-92-0; **8**, 113810-79-0; **10a**, 72474-00-1; **10b**, 50397-92-7; **10c**, 113810-83-6; **10d**, 1128-08-1; AlBu-i_3, 100-99-2; $AlPh_3{\cdot}OEt_2$, 58482-37-4; i-$Bu_2AlCH{=}CH(CH_2)_3CH_3$, 26076-75-5; i-$Bu_2AlCH{=}CH(CH_2)_2CH_3$, 83021-61-8; 5-hexene-2-one, 109-49-9.

exo,endo-3-((Dimethylamino)methyl)-*d*-camphor: *d*-Camphor Mannich Products

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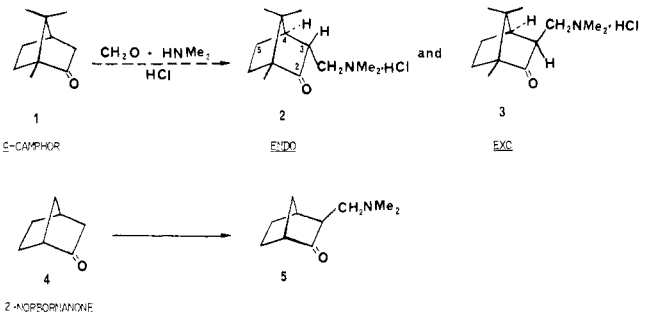
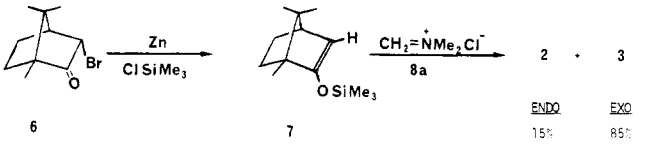
Of the two 3-((dimethylamino)methyl) Mannich products from *d*-camphor (**1**), the endo product (**2**) has been described by Hine and co-workers.[3,4] Several other reports[5] on reactions to give these products fail to consider the stereochemistry of the reaction and do not adequately characterize the product or product mixtures. It appears, however, that the exo compound **3** has not been previously described. Here we consider the synthesis and properties of this exo diastereomer **3**, its configurational assignment, and its equilibration with the endo isomer via the enolate anion.

Although the classical conditions for the Mannich condensation[6] (CH_2O + $HNMe_2{\cdot}HCl$) work well for the unsubstituted 2-norbornanone[7] (**4**) to give the less hindered exo isomer **5**, these conditions are not applicable to the more hindered camphor. *exo*-3-((Dimethylamino)-

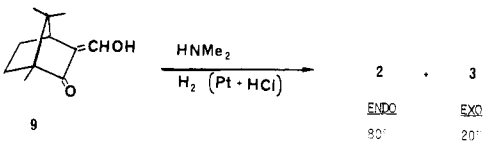


methyl)-*d*-camphor (**3**) has now been prepared by the reaction of dimethylmethyleneammonium chloride[8] (**8a**) or dimethylmethyleneammonium iodide (**8b**, Eschenmoser's salt[9]) in acetonitrile solvent with the trimethylsilyl enol ether[10] (**7**) of *d*-camphor, which was prepared from *endo*-(+)-3-bromo-*d*-camphor (**6** → **7**). The crude product



from the reaction of **7** with **8a** ($CH_2{=}NMe_2{}^+Cl^-$) is a mixture of endo and exo isomers (**2** and **3**) in approximately 15:85 ratio (as determined from the well-separated 400-MHz NMR signals of the H-3 and H-4 protons of the exo and endo isomers as either the salts or free bases; cf. Table I). Crystallization gave the purified exo isomer (mp 219–220 °C) in an isolated yield of 66%. The same reaction using dimethylmethyleneammonium iodide (**8b**, Eschenmoser's salt) gave an 86% yield of crude *exo*-hydroiodide (**3**·HI) that contained less than 3% of the endo isomer.

The procedure used by Hine and co-workers,[3,4,5b] in which 3-(hydroxymethylene)-*d*-camphor[11] (**9**) was treated



with dimethylamine followed by hydrogenation in the presence of platinum oxide and hydrochloric acid,[12] gave a 90% yield of a 4:1 mixture of isomers (**2**·HCl/**3**·HCl). Repeated crystallations of these hydrochlorides gave a single product, mp 208–209 °C. Hine and co-workers assigned the endo configuration, **2**, to this product based on its proton NMR spectra. We have verified this assignment and have made the exo assignment to the other isomer based on decoupling studies on the hydrochlorides and free bases of both **2** and **3** as given in Table I. The rigid camphor system permits the application of the Karplus equation[13a] to these isomers with confidence. The dihedral angle between H-3 and H-4 in the exo isomer is close to 90° and no appreciable coupling of these protons would be expected. This is observed for the major isomer prepared from the silyl enol ether, **7**, and the minor isomer obtained from the hydroxymethylene derivative **9**. The corresponding angle between H-3 and H-4 in the endo isomer is about 30° for which a coupling constant of 3–4 Hz would be expected, as is observed for the major isomer obtained from **9**. Furthermore, as expected, a long-range coupling between H-3 and H-5β was observed in the endo isomer (as the base **2** or salt **2**·HCl or **2**·HI) by virtue of the "W" configuration[14] of these protons. No such coupling was observed for the major isomer (**3**) prepared from the silyl enol ether.

(1) McClure, Natalie L. Ph.D. Thesis, Stanford University, 1979.
(2) On leave from the Department of Chemistry, Xuzhou Teachers' College, Xuzhou, Jiangsu, PRC.
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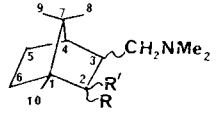
Table I. ^{1}H NMR Data:[a] Chemical Shifts (δ) and Couplings (J, Hz) for Compounds 2, 3, 10, and 11[a,b]



compd	CH_2N	H-3	H-4	H-5β	H-5α	H-6α	H-6β	NMe_2	Me-8,9,10
2·HCl (3-*endo*-; R, R′ = O)	A 3.13 } m (3.08–3.17) B 3.12 } J_{11A-B} = 7 $J_{11-3} \cong$ 3	3.07 m $J_{3-11} \cong$ 3 J_{3-4} = 4 $J_{3-5\beta} \cong$ 1.5	2.62 t $J_{4-3} \cong$ 4 $J_{4-5\beta} \cong$ 4	1.96 m[c] $J_{5\beta-4} \cong$ 4 $J_{5\beta-3} \cong$ 1.5	1.77 dt (1.82–1.73)	1.44 m[c] (1.44–1.39)	1.23 m[c] (1.28–1.19)	2.85 s	1.04 s 0.97 s 0.94 s
2·base (3-*endo*-; R, R′ = O)	A 2.51 dd B 2.41 dd J_{11A-B} = 12 J_{11A-3} = 4.8 J_{11B-3} = 10.7	2.63 m J_{3-11A} = 12 J_{3-11B} = 4.8 J_{3-4} = 4.6 $J_{3-5\beta} \cong$ 1.5	2.16 t J_{4-3} = 4.6 $J_{4-5\beta}$ = 4.3	1.83 m (1.78–1.88) coupled to 3, 4, 5α, 6α, 6β protons	1.68 dt (1.64–1.73) coupled to 5β, 6α, 6β protons	1.58 m[c] (1.53–1.62)	1.26 m[c] (1.22–1.34)	2.25 s	1.00 s 0.92 s 0.88 s
3·HCl (3-*exo*-; R, R′ = O)	A 3.13 m[c] B 3.09 J_{11A-B} = 1.3 J_{11-3} = 4	2.50 t J_{3-11A} = 4.5 J_{3-11B} = 4.5	2.40 d $J_{4-5\beta}$ = 4.3	2.09 m (2.05–2.15) coupled to 4, 5α, 6α, 6β protons	1.72 m (1.64–1.77) coupled to 4, 5β, 6 protons	1.68 m	1.56 m $J_{6\beta-6\alpha}$ = 14 $J_{6\beta-5\alpha}$ = 5	2.84 s	0.98 s 0.92 s 0.72 s
3·HI (3-*exo*-; R, R′ = O)	A 3.23 dd B 3.09 dd J_{11A-B} = 13 J_{11A-3} = 4 J_{11B-3} = 4	2.61 t J_{3-11A} = 4 J_{3-11B} = 4	2.46 d $J_{5\beta-4}$ = 4.0	2.10 m	1.76 m (1.68–1.78)	1.71 m	1.57 m (1.50–1.61)	2.78 s	0.97 s 0.92 s 0.73 s
3·base (3-*exo*-; R, R′ = O)	A 2.66 dd B 2.39 dd J_{11A-B} = 12 J_{11A-3} = 3 J_{11B-3} = 7	2.01 q J_{3-11A} = 3 J_{3-11B} = 7	2.05 d $J_{4-3} \cong$ 0 $J_{4-5\beta}$ = 4	ca. 1.99 m	1.65 m (1.61–1.70)	1.50 m (1.46–1.54)	1.43 m (1.39–1.46)	2.25	0.94 s 0.92 s 0.78 s
10·HCl[d,e] (3-*exo*-, 2-*exo*-; R′ = OH, R = H)	A 3.77 t B 2.84 t J_{11A-B} = 12 J_{11A-3} = 12 J_{11B-3} = 1	2.05 m[c] J_{3-11A} = 12 J_{3-11B} = 1 J_{3-2} = 6.4	1.47 d $J_{4-5\beta}$ = 4.3	1.76 tt $J_{5\beta-4}$ = 4.3 $J_{5\beta-5\alpha}$ = 7.8 $J_{5\beta-6\alpha}$ = 2.8 $J_{5\beta-6\beta}$ = 7.2	1.50 td $J_{5\alpha-5\beta}$ = 7.8 $J_{5\alpha-6\alpha}$ = 12.5 $J_{5\alpha-6\beta}$ = 3.7	(1.20 m to 1.04 m) not coupled to proton C-2 H		2.83 t J_{+NH} = 5	1.03 s 0.94 s 0.80 s
11·HCl[e,f] (3-*exo*-; R = OH, R′ = benzyl)	A 2.96 m[c] B 2.73 dq J_{AB} = 18 J_{A-3} = 10 J_{B-3} = 3	2.04 dd J_{3-11A} = 10 J_{3-11B} = 3	2.14 d[f] $J_{4-5\beta}$ = 4.4 not coupled to C-3 H	1.94 tt	1.79 m[c]	1.53 qd	1.28 m[c]	2.51 d J_{+NH} = 5	1.17 s 0.88 s 0.76 s

[a] Chemical shift values downfield from TMS. See Experimental Section for instrumental details, solvents, abbreviations, etc. Coupling constants were determined by complete proton decoupling. Each signal integrated for the indicated number of protons within experimental error. [b] Signals from OH peaks were determined by deuterium exchange. [c] This multiplet was relatively sharp, with seven peaks apparently an overlapping doublet of quartets. [d] The C-2 proton, 4.18 ppm, was coupled to the C-3 proton (J = 6.4 Hz); it was not coupled to the C-6 β-proton. The OH proton, 4.04 ppm, was coupled to the C-2 proton (J = 6.4 Hz). [e] The two benzylic protons, at 3.09 and 2.88 ppm, were coupled (J_{AB} = 13.6 Hz); the five aromatic protons were at 7.0–7.3 ppm. The stereochemistry at C-2 in **11** is not revealed by these spectra. [f] No coupling of the C-3 and C-4 protons is evident.

Table II. ^{13}C NMR Data: Chemical Shifts (δ ($CDCl_3$)) for Compounds 1, 2, and 3

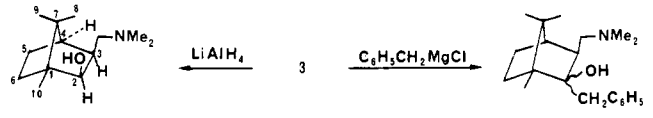
carbon atom	2 (*endo*)	3 (*exo*)	1[a]	1[b]
C(2)	222.6	222.9	218.6	218.4
C(11)	59.8	59.7		
C(1)	56.3	58.4	57.4	57.4
C(4)	49.9	50.1	43.6	43.2
C(3)	46.6	48.6	43.2	43.1
C(7)	46.4	47.7	46.8	46.6
$N(CH_3)_2$	44.2, 43.8	43.8, 43.5		
C(5)	31.3	29.2	27.3	27.0
C(6)	20.6	28.4	30.2	29.9
C(8)	19.4	21.1	19.9	19.7
C(9)	18.9	19.8	19.3	19.1
C(10)	9.3	9.3	9.5	9.2

[a] Proton noise decoupled ^{13}C spectra taken with a Varian FT400 instrument (100.58 MHz); $CDCl_3$ solvent; chemical shift δ relative to dioxane at 67.3 ppm. [b] Morris, D. G.; Murray, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1579–1584.

Holy et al.[5c] studied the formation of Mannich products from the enolate anion of ketones using potassium hydride followed by treatment with Eschenmoser's reagent (**8b**). From the published data, it is not possible to determine which isomer was formed from camphor. We have repeated this preparation and found in one experiment a 1:4 ratio of exo:endo isomers in an isolated yield of 60%. This is essentially the equilibrium mixture. The pure endo isomer was obtained by several recrystallizations from pentane.

Isomers **2** and **3** have been equilibrated via the enolate anion (CD_3OD + NaOD) to give an exo:endo ratio of about 4:1. Clearly the endo isomer is the thermodynamically more stable, as would be predicted based on steric considerations.[15] Therefore, the reaction to produce the exo isomer **3** in excess from the trimethylsilyl enol ether **7** with either **8a** or **8b** in acetonitrile at 20 °C is kinetically controlled.

The $LiAlH_4$ reduction prouct **10** of **3** has an H-2/H-3 coupling of 6.9 Hz. This is consistent with the cis-2-endo/3-endo proton arrangement but incompatible with a cis-2-exo/3-exo or trans-2/3 proton arrangement.[13] In addition, neither H-2 nor H-3 in the reduction product **10** shows a long-range coupling.[13b,14] These NMR data, taken together with the known preferential endo face attack of $LiAlH_4$ (camphor gives isoborneol), support the assigned exo configuration of the (dimethylamino)methyl group in **3** as well as in **10**.



10 11

Reaction of benzylmagnesium chloride with the exo isomer **3** gives adduct **11**, in which the stereochemistry at C-2 is not defined. Mechanistic considerations can be advanced for either configuration at C-2. Proton NMR does not give any evidence because of the lack of a hydrogen on C-2. However, it is clear, because of the lack of H(3)/H(4) coupling in **11**, that the (dimethylamino)-methyl group at C-3 has retained its exo configuration.

Both **10** and **11** were used in an exploratory search for an improved chiral ligand for asymmetric reductions by chiral lithium aluminum alcoholates ($LiAlH_x(OR^*)_{4-x}$) in analogy with our previous studies.[1,16] These ligands were two of a number of such chiral carbinol amines studied in the asymmetric reduction of acetophenone. They were not very effective as shown in Table III, and additional analogues were not prepared.

Table III. Asymmetric Reductions of Acetophenone by Amino Carbinols[a] 10 and 11

$$LiAl(OR^*)_xH_y + PhC(O)CH_3 \rightarrow \xrightarrow{H_3O^+} {}^{*}PhCHOHCH_3$$

reagent	molar ratio[b] reagent:$LiAlH_4$	product % ee (config)	yield,[c] %
10	1:1	6 (*S*)	77
	2:1	13 (*R*)	77
	3:1	35 (*R*)	72
11	1:1	3 (*R*)	97
	2:1	27 (*R*)	95
	3:1	29 (*R*)	82

[a] Data from ref 1. [b] The amount of acetophenone was 0.8 mol % of the $LiAlH_4$ taken. [c] These are isolated yields by preparative gas chromatography; % ee determined by optical rotation (cf. Experimental Section).

Experimental Section

Materials and Methods. The synthetic procedures and methods for the asymmetric reductions are described in the thesis of N.L.M.[1] All ^1H NMR measurements have been retaken on a Varian FT 400-MHz instrument with complete decoupling in $CDCl_3$ solvent. Hydroxyl protons were identified by deuterium exchange. Chemical shifts (δ) are given in ppm relative to $SiMe_4$ (TMS). Signal multiplicities are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (*J*) are in hertz (Hz). Melting points were determined between cover glasses on a microscope hot stage. Optical rotations (to 0.001°) were taken on a Rudolph Autopol III electronic instrument in 10-cm cells with permanent end plates, thermostated at 20.0 ± 0.1 °C. Reactions were routinely followed by using silica gel GF thin-layer chromatography (TLC) plates (250 μm, Analtech). Products were visualized by UV and/or by dipping into a 7% solution of phosphomolybdic acid in ethanol followed by heating to 150 °C. All moisture-sensitive reactions were done in oven-dried (200 °C) equipment under a dry N_2 atmosphere with transfer or introduction of solutions via syringe or cannula through a serum stopper. Freshly distilled solvents were stored over 3A molecular sieves activated at 300 °C.

(+)-3-*exo*-((Dimethylamino)methyl)-*d*-camphor [(1*R*,3*S*,4*R*)-(+)-3-((Dimethylamino)methyl)camphor] (3). *d*-Camphor trimethylsilyl enol ether (**7**, 8.9 g, 40 mmol), prepared from *endo*-(+)-3-bromo-*d*-camphor,[15] dissolved in 50 mL of anhydrous ether was added to a solution of dimethylmethyleneammonium chloride[8] (**8a**, 4.35 g, 40 mmol) in anhydrous acetonitrile (50 mL) at 20 °C. After 12 h the mixture was treated with dilute HCl (15 mL, 7%). The aqueous layer was separated and made basic, and the amine was extracted with ether (3 × 50 mL). Gaseous HCl was bubbled into the dried ($MgSO_4$) ether layer to give hydrochloride (**3**·HCl, 7.86 g, 80%). After recrystallization from acetone: platelets, 6.5 g, mp 219–220 °C. A subsequent sample with the same melting point had the following properties: $[\alpha]^{20.0}_D$ +67.2° (*c* 2.6, CH_3OH); CD $[\theta]_{292}$ +5960 (CH_3OH). Anal. Calcd for $C_{13}H_{24}NOCl\cdot H_2O$: C, 59.19; H, 9.93; N, 5.31; Cl, 13.44. Found: C, 59.66; H, 9.70; N, 5.30; Cl, 13.75. The hydrochloride was converted to the free base (3% NH_4OH): colorless oil; $[\alpha]^{20.0}_D$ +50 ± 1° (*c* 1.5, CH_3OH). Anal. Calcd for $C_{13}H_{23}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.69; H, 11.90; N, 6.51. The ^1H NMR data for the hydrochloride (**3**·HCl) and free base (**3**) are given in Table I, and the ^{13}C NMR for **3**·HCl are listed in Table II.

d-Camphor trimethylsilyl enol ether (**7**) was treated with dimethylmethyleneammonium iodide (Eschenmoser's salt[9]) in acetonitrile. The resulting light yellow solid (86% yield of crude

(15) Woods, W. G.; Roberts, J. D. *J. Org. Chem.* **1957**, *22*, 1124–1126. The configuration of *endo*-3-bromocamphor has been unequivocally established by an X-ray crystal determination.

(16) (a) Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 1870–1877. (b) Reich, C. Ph.D. Thesis, Stanford University, 1976.

hydroiodide of exo isomer **3**, mp 208–212 °C) was shown by NMR to contain less than 3% of the endo isomer. Recrystallization (EtOAc) gave platelets: mp 216–220 °C; $[\alpha]^{20.0}_D$ +53 ± 0.5° (*c* 1.9, CH_3OH). Anal. Calcd for $C_{13}H_{24}NOI$: C, 46.30; H, 7.17; N, 4.15. Found: C, 46.26; H, 7.05; N, 4.24.

(+)-3-*endo*-((Dimethylamino)methyl)-*d*-camphor [(1*R*,3*R*,4*R*)-(+)-3-((Dimethylamino)methyl)camphor] (2). *d*-Camphor was treated with potassium hydride in THF followed by Eschenmoser's salt[9] by the method of Poulter and co-workers[5d] as described by Holy et al.[5c] The crude product (60% yield) was an 80:20 mixture of endo:exo isomers (free bases). Crystals were obtained from this oil at −15 °C in pentane; recrystallization gave the purified endo base (mp 34–36 °C, $[\alpha]^{20.0}_D$ +77.4 ± 1° (*c* 0.5, CH_3OH)), which retained about 3% of the exo isomer as shown by the NMR spectrum (1.95–2.10 ppm, area for $H_3 + H_4 + H_{5\beta}$ exo isomer, versus 2.58–2.68 ppm, area for H_3 endo isomer). This was converted to the hydrochloride: mp 211–212 °C dec; $[\alpha]^{20.0}_D$ +31 ± 1° (*c* 0.5, CH_3OH).

We have repeated the procedure used by Hine et al.[3] for synthesis of **2**. 3-(Hydroxymethylene)-*d*-camphor[11] (**9**) was treated with aqueous dimethylamine to give 3-((dimethylamino)-methylene)-*d*-camphor (bp 118–120 °C (3.5 Torr)) as a waxy solid (mp 50–52 °C) in 90% yield. This crude product in methanol was hydrogenated at 1–2 atm using 10% Pd–C catalyst in the presence of a slight excess of HCl added in small amounts as the reduction progressed. The product was a solid (mp 200–206 °C dec), which by NMR was an 80:20 mixture of endo:exo isomers. Several crystallizations from EtOH–EtOAc gave the purified endo hydrochloride isomer, (mp 211–212 °C dec). This hydrochloride was converted to the crystalline free base identical with that described above. The NMR spectra of the endo hydrochloride and endo free base **2** are given in Table I. The crude sample from this reaction corresponded in NMR and melting point to that of a corresponding sample supplied by Professor Hine.[12]

(1*R*,2*R*,3*S*,4*R*)-3-((Dimethylamino)methyl)isoborneol Hydrochloride (10·HCl). *exo*-3-((Dimethylamino)methyl)-*d*-camphor (**3**, 2.6 g, 12 mmol) in anhydrous ether (25 mL) was added slowly to an ether solution of $LiAlH_4$ (12 mL of 1.0 M + 75 mL of ether) at 20 °C. After 12 h, saturated NH_4Cl solution (2 mL) was added and the mixture filtered. The combined ether layer and extracts of the salts were extracted with 10% HCl. The acid extracts were made basic and extracted with ether; these extracts were dried ($MgSO_4$) and treated with dry HCl gas to give the HCl salt (**10**·HCl, 2.14 g, 72% yield), which was recrystallized from acetone: mp 259–61 °C dec; $[\alpha]_D^{27}$ +57.9° (*c* 0.88, MeOH). Anal. Calcd for $C_{13}H_{26}NOCl$: C, 63.01; H, 10.57; N, 5.65. Found: C, 62.74; H, 10.47; N, 5.49.

This salt was converted to the free base with dilute ammonia to give a clear oil. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.69; H, 11.90; N, 6.51.

(1*R*,2*R*,3*S*,4*R*)-2-Benzyl-3-((dimethylamino)methyl)isoborneol (11). To an ether solution (25 mL) of Grignard reagent prepared from benzyl chloride (1.05 g, 8.3 mmol) was added *exo*-3-((dimethylamino)methyl)-*d*-camphor (**3**, 1.45 g, 6.9 mmol) in ether (75 mL). After 24 h at 20 °C the mixture was hydrolyzed (saturated NH_4Cl) and worked up, and the crude product (containing some unreacted **3**) was crystallized (EtOAc) to give 2-benzyl-3-((dimethylamino)methyl)isoborneol (**11**) hydrochloride: 0.80 g, 47% yield; mp 205–206 °C; $[\alpha]^{29}_D$ −7.55° (*c* 0.53, CH_3OH); NMR, Table I. This was converted to the free base to give a clear oil: 0.59 g, 88% yield. Anal. Calcd for $C_{20}H_{31}NO$: C, 79.68; H, 10.36; N, 4.64. Found: C, 79.76; H, 10.52; N, 4.57.

Equilibration of *endo*- and *exo*-3-((Dimethylamino)-methyl)-*d*-camphor. A purified sample of exo isomer **3** (free base) was dissolved in a 2% sodium methoxide solution in methanol at 20 °C. Aliquots were removed at intervals, the 3-((dimethylamino)methyl)-*d*-camphor was recovered as the free base, and the ratio of endo:exo isomers was determined by comparison of the integration of signals at 1.95–2.10 ppm, representing $H_3 + H_4 + H_{\beta 5}$ of the exo isomer, versus those at 2.14–2.20 ppm, representing H_4, or 2.58–2.68 ppm for H_3 of the endo isomer. Within 48 h the exo isomer was converted to a constant mixture of approximately 80:20 endo:exo. Starting with the pure endo isomer, the same 80:20 exo ratio was attained in 24 h.

Asymmetric Reductions with Lithium Aluminum Alkoxy Hydride Derived Reagent[1] from 10 and 11 (Table III). The asymmetric reductions were performed in an oven-dried 4-dram vial equipped with a serum stopper and a magnetic stirring bar. A dry argon atmosphere was maintained through a syringe needle inlet and outlet through a Drierite drying tube. A standard $LiAlH_4$ solution (about 0.2 mL, 0.2 mmol, of 1.0 M solution) was introduced via syringe. To this solution at 0 °C was introduced via syringe an ether solution of **10** or **11** as the free base. Approximately 1 mL containing a known molar equivalent of the carbinol amine **10** or **11** was introduced over a 30-s interval. In these cases a clear solution resulted. After 6.5 min an ether solution of acetophenone (0.8 molar equivalent to the $LiAlH_4$ at 0 °C) was injected, and the reaction mixture was stirred at 0 °C for 3 h. The reaction was hydrolyzed (2 mL, 1 N HCl) and extracted (ether). The ether extracts were dried ($MgSO_4$) and concentrated to give a colorless oil, which was weighed and then analyzed and preparatively purified by gas–liquid chromatography (GLC). The optical rotation of the GLC-purified methylphenylcarbinol was taken by using $[\alpha]^{20.0}_D$ 43.7° (*c* 1, CH_3OH) as the value for enantiomerically pure methylphenylcarbinol. The reliability of this determination was verified by use of the α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA-Cl) reagent.[17] The results are summarized in Table III.

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Registry No. **1**, 464-49-3; **2**, 33162-70-8; **2**·HCl, 33162-71-9; **2**·HI, 114027-32-6; **3**, 113890-52-1; **3**·HCl, 27058-64-6; **3**·HI, 113972-49-9; **6**, 10293-06-8; **7**, 70982-26-2; **8a**, 30354-18-8; **8b**, 33797-51-2; **9**, 14681-31-3; **10**, 113890-53-2; **10**·HCl, 113972-50-2; **11**, 113812-33-2; **11**·HCl, 113812-34-3; $PhCOCH_3$, 98-86-2; (*R*)-$PhCHOHCH_3$, 1517-69-7; (*S*)-$PhCHOHCH_3$, 1445-91-6; 3-((dimethylamino)methylene)-*d*-camphor, 113890-54-3.

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Synthesis of Cyclopenta[*cd*]pyrene and Its Benzannelated Derivative Naphtho[1,2,3-*mno*]acephenanthrylene

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Characterization of cyclopenta[*cd*]pyrene as an important component of kerosene and gasoline soots[1-3] and its identification as a potent mutagen[4] and cell-transforming agent[5,6] have evoked considerable interest in peripherally fused cyclopenta-polycyclic aromatic hydrocarbons (cyclopenta-PAH) as potential environmental carcinogens. Cyclopenta[*cd*]pyrene is distinguished from most other

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