7,7-Dimethylenebicyclo[2.2.1]hept-5-ene (11).—Purification of 11, bp 57–60° (50 mm) [lit.[16] bp 63° (60 mm)], was accomplished by vpc (silicone oil column at 98°): ir[30] (CCl_4) 3100 (w), 3020 cm^{-1} (w); nmr (CCl_4) 3.97 (t, H-5,6, sp 2 Hz), 7.92 (br, H-1,4), 8.22 (m, H-2,3 exo), 8.98 (m, H-2,3 endo), 9.62 (m, H cyclopropyls anti), 9.71 (m, H cyclopropyls syn).

7,7-Dimethylenebicyclo[2.2.1]hepta-2,5-diene (12).—Purification of 12, bp 30–31° (18 mm) [lit.[16] bp 37° (20 mm)], was achieved by vpc using a silicone oil column at 91°: ir[30] (CCl_4) 3100, 3010 cm^{-1} (w); nmr[29] (CCl_4) 3.26 (t, H-2,3,5,6, sp 2 Hz), 7.08 (t, H-1,4, sp 2 Hz), 9.57 (s, H cyclopropyls).

Registry No.—**1a,** 35092-24-1; **1b,** 35129-58-9; **2a,** 35092-25-2; **2b,** 35092-26-3; **3a,** 35092-27-4; **3b,** 35092-28-5; **5a,** 35092-29-6; **6a,** 35092-30-9; **6b,** 35092-31-0; **7a,** 35092-32-1; dimethylfulvene, 2175-91-9; vinylene carbonate, 872-36-6.

Preparation and Stereochemistry of 1-Methyl-2-methylenebenzonorbornene and 1,2-Dimethyl-2-benzonorbornenyl Derivatives

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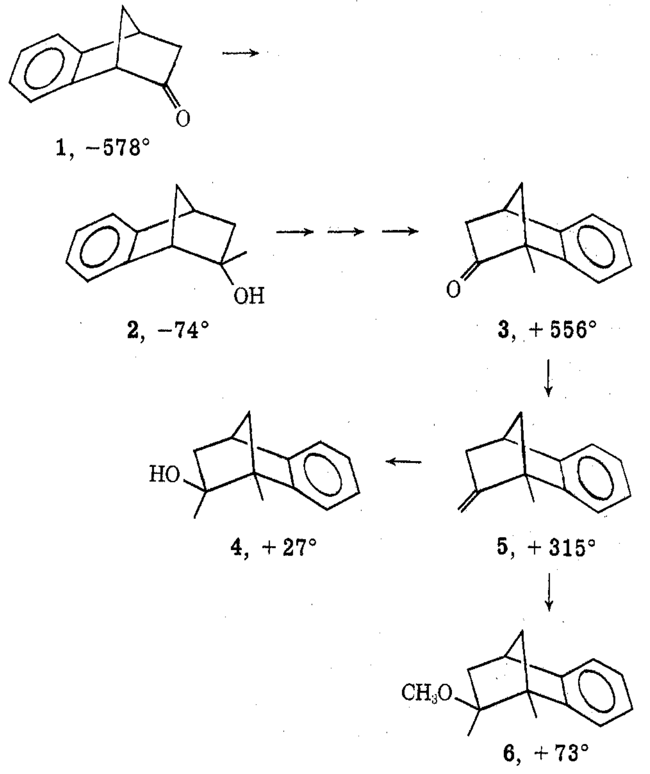
Optically active 2-benzonorbornenone (1) has been converted to active 1-methyl-2-methylenebenzonorbornene (5) in five steps and the latter has been converted to active 1,2-dimethyl-*exo*-2-benzonorbornenol (4) and 1,2-dimethyl-*exo*-2-benzonorbornenyl methyl ether (6). Absolute configurations and rotations of 4, 5, and 6 are established by correlation with 1.

We have recently investigated the symmetry properties of ionic intermediates in the 1,2-dimethyl-2-benzonorbornenyl system[1] This paper reports our synthetic entry into this system and the correlation of optical configurations and rotations required for that investigation.

The 1,2-dimethyl-*exo*-2-benzonorbornenyl system was derived from 2-benzonorbornenone (1)[2] as outlined in Chart I. The key intermediate in this synthesis is 1-methyl-2-methylenebenzonorbornene (**5**), which was prepared from 1-methyl-2-benzonorbornenone (3) by the Wittig reaction. The latter was prepared from 1 by the series of reactions used earlier[3,4] to convert norcamphor to 1-methyl-2-norbornanone. This sequence involves conversion of 1 to 2-methyl-*endo*-2-benzonorbornenol (2) with methylmagnesium bromide followed by acid-catalyzed rearrangement of 2 in acetic acid to 1-methyl-*exo*-2-benzonorbornenyl acetate. This step results in configurational change of the bicyclic system, as illustrated in Chart I. Reductive cleavage of the acetate with lithium aluminum hydride followed by Oppenauer oxidation[5] of the resulting 1-methyl-*exo*-2-benzonorbornenol gave **3**.

CHART I



Absolute configurations and rotations[6] are shown in Chart I. These were determined directly starting with optically active 1. The absolute configuration and rotation of the latter had been established earlier.[2] Optically active 1 was prepared[2] by asymmetric hydroboration of benzonorbornadiene with tetraisopinocamphenyldiborane[7] followed by oxidation of the resulting active *exo*-2-benzonorbornenol. The most active samples were about 68% optically pure.

Optically active **5** was converted to active 1,2-dimethyl-*exo*-2-benzonorbornenol (4) by oxymercuration–demercuration[8] and to active 1,2-dimethyl-*exo*-2-benzonorbornenyl methyl ether (6) by methoxymercuration–demercuration.[9] There is evidence[3,7] that this type of addition does not result in rearrangement in a similar system, and from this and the reproducible changes in rotations, we conclude that these transformations do not result in loss of optical purity.

Experimental Section

Materials.—Racemic and optically active 2-benzonorbornenone (1) were prepared in about 80% yield from benzonorborna-

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[1] H. L. Goering and J. V. Clevenger, to be submitted for publication.

[2] D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, **90**, 4877 (1968).

[3] H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and H. Humski, *J. Org. Chem.*, **34**, 624 (1969).

[4] J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

[5] P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

[6] Rotations are for chloroform solutions at 25°.

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

[8] H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967), and references cited therein.

[9] H. C. Brown and M.-H. Rei, *ibid.*, **91**, 5646 (1969).

diene[10] as described earlier.[2] This method involves hydroboration with diborane in tetrahydrofuran for racemic products or with tetraisopinocamphenyldiborane in diglyme for active products, followed by oxidation of the resulting *exo*-2-benzonorbornenol. Asymmetric hydroboration with tetraisopinocamphenyldiborane[2,7] derived from (−)-α-pinene, $[\alpha]^{20}_{\mathrm{D}}$ −46.7° (neat) (~91% optically pure[2]), led to (−)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ −368° (c 1.25, isooctane) (~65% optically pure[2]). Similar results were obtained with (+)-pinene, $[\alpha]^{25}_{\mathrm{D}}$ 40.2° (neat). In this case (+)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ 321° (isooctane), was obtained. For several preparations the optical purity of **1** was about 70% of that of the pinene.

2-Methyl-*endo*-2-benzonorbornenol (**2**).—A solution of 24.8 g (0.157 mol) of 2-benzonorbornenone (**1**) in 35 ml of ether was slowly added to 62.5 ml (0.187 mol) of 3 M methylmagnesium bromide in ether. During the addition the reaction flask was cooled with an ice bath. After the solution was stirred for an additional 1 hr at room temperature, saturated aqueous ammonium chloride was added, after which the clear ether solution was decanted from the precipitate. The solid material was washed with ether and the extracts were combined, dried (magnesium sulfate), and concentrated to dryness under reduced pressure. The yield of crude solid 2-methyl-*endo*-2-benzonorbornenol (**2**) was 26.5 g (97%). Recrystallization from pentane gave pure **2**, mp 61–62°. The nmr spectrum had an aromatic multiplet at τ 2.56–3.12 (4 H), a bridgehead proton (C-4) multiplet at τ 6.68–6.88 (1 H), a bridgehead proton (C-1) multiplet at τ 6.86–7.10 (1 H), methylene and hydroxyl absorption at τ 7.82–9.12 (5 H), and a methyl singlet at τ 8.48 (3 H).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.53; H, 7.93.

By the above procedure 36 g of (−)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ −391° (c 2.32 $CHCl_3$), $[\alpha]^{25}_{\mathrm{D}}$ −385 (isooctane) (68% optically pure[2]), was converted to 40 g of (−)-**2**. A pure sample of (−)-2-methyl-*endo*-2-benzonorbornanol (**2**), mp 58–71°, $[\alpha]^{25}_{\mathrm{D}}$ −50.0° (c 9.19, $CHCl_3$), was obtained by preparative gc (20% KOH, 1% Carbowax 40 M on firebrick) followed by sublimation.[11] This corresponds to an absolute rotation of about $[\alpha]^{25}_{\mathrm{D}}$ −74° ($CHCl_3$) for **2**.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.72; H, 8.11.

1-Methyl-2-benzonorbornenone (**3**).—A solution of 26.5 g (0.152 mol) of **2** in 67 ml of acetic acid was treated with 1 ml of sulfuric acid and 0.5 ml of water. The resulting purple solution was heated at 100° for 1 hr and then poured onto 200 g of ice. A solution of 40 g (1 mol) of sodium hydroxide in 200 ml of water was alowly added, after which saturated sodium carbonate solution was added to completely neutralize the reaction mixture. The mixture was extracted with ether. After drying, the ether was removed under reduced pressure, leaving 31.2 g (95%) of crude 1-methyl-*exo*-2-benzonorbornenyl acetate as a brown oil. Gas chromatography showed that this acetate fraction consisted of ~80% 1-methyl-*exo*-2-benzonorbornenyl acetate.

The crude acetate was taken up in 60 ml of dry ether and reduced with 5.08 g (0.134 mol) of lithium aluminum hydride. After work-up in the usual manner, 24.6 g of crude solid 1-methyl-*exo*-2-benzonorbornenol was obtained. Gas chromatography indicated that this material was about 80% pure and contained about 10% each of two other components.

The crude 1-methyl-*exo*-2-benzonorbornenol was oxidized to 1-methyl-2-benzonorbornenone (**3**) with p-benzoquinone and aluminum *tert*-butoxide by a procedure described earlier.[2,5] The crude product was shown to be 86% **3** by analytical gc. A pure sample of **3** was obtained by preparative gc (30% cyanosilicone XF-1150 on Chromosorb). The nmr spectrum exhibited absorptions at τ 2.80–3.13 (m, Ar H, 4 H), 6.42 (m, C-4 H, 1 H), 7.53–8.48 (m, CH_2, 4 H), and 8.60 (s, CH_3, 3 H).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.80; H, 7.12.

By the above procedure 34 g (0.195 mol) of (−)-**2**, derived from 68% optically pure (−)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ −391° (c 2.32, $CHCl_3$), was converted to 23.3 g (69%) of (+)-1-methyl-2-benzonorbornenone (**3**), which after purification (gc) had $[\alpha]^{25}_{\mathrm{D}}$ 376° (c 4.74, $CHCl_3$[11]). This corresponds to an absolute rotation of about $[\alpha]^{25}_{\mathrm{D}}$ 556° ($CHCl_3$) for **3**.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.70; H, 7.14.

1-Methyl-2-methylenebenzonorbornene (**5**).—This compound was prepared from 1-methyl-2-benzonorbornenone (**3**) by the procedure[3] used to prepare 1-methyl-2-methylenenorbornane from 1-methyl-2-norbornanone. In a typical experiment 19.9 g (0.114 mol) of **3** gave 16.5 g of crude **5**. Fractionation with a spinning-band column gave 13 g (67%) of 1-methyl-2-methylenebenzonorbornene, bp 52–53° (0.1 mm). The nmr spectrum had an aromatic multiplet at τ 2.78–3.10 (4 H), olefin proton triplets at τ 5.11 with $J = 3.3$ Hz (1 H) and 5.31 with $J = 3.3$ Hz (1 H), a bridgehead proton multiplet at τ 6.62–6.82 (1 H), a methylene multiplet at τ 7.13–8.37 (4 H), and a methyl singlet at τ 8.43 (3 H).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.73; H, 8.11.

Optically active 1-methyl-2-methylenebenzonorbornene (**5**) was prepared from active 2-benzonorbornenone (**1**) without purification of the intermediates. In one experiment 23.4 g (0.148 mol) of (−)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ −368° (c 1.25, isooctane) (~64% optically pure[2]), gave 12.63 g (50%) of (+)-1-methyl-2-methylenebenzonorbornene (**5**), $[\alpha]^{25}_{\mathrm{D}}$ 202° (c 2.72, $CHCl_3$). In another case (+)-**1**, $[\alpha]^{25}_{\mathrm{D}}$ 292° (isooctane), gave (−)-1-methyl-2-methylenebenzonorbornene (**5**), $[\alpha]^{25}_{\mathrm{D}}$ −163° (c 2.63, $CHCl_3$).[11] These results indicate an absolute rotation of about $[\alpha]^{25}_{\mathrm{D}}$ 315° ($CHCl_3$) for **5**.

1,2-Dimethyl-*exo*-2-benzonorbornenol (**4**).—Oxymercuration–demercuration of **5** according to a previously described procedure[12] gave **4** in 97% yield. The crude product was ~96% pure according to gc. Sublimation at 80° (14 mm) gave pure **4**, mp 54–55.5°. The nmr spectrum had an aromatic multiplet at τ 7.67–8.50 (4 H), a bridgehead proton multiplet at τ 6.73–6.96 (1 H), methylene absorption at τ 7.67–8.50 (5 H), and methyl singlets at τ 8.60 (3 H) and 9.18 (3 H).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.70; H, 8.45.

By the above procedure (+)-**5**, $[\alpha]^{25}_{\mathrm{D}}$ 213° ($CHCl_3$), was converted to (+)-1,2-dimethyl-*exo*-2-benzonorbornenol (**4**), which after purification by gc (20% KOH, 1% Carbowax 40M on firebrick) and sublimation had mp 62–63°, $[\alpha]^{25}_{\mathrm{D}}$ 18.45° (c 5.92, $CHCl_3$).[11] This corresponds to an absolute rotation of about $[\alpha]^{25}_{\mathrm{D}}$ 27° ($CHCl_3$) for **4**.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.11; H, 8.55.

(+)-1,2-Dimethyl-*exo*-2-benzonorbornenyl Methyl Ether (**6**). Optically active 1-methyl-2-methylenebenzonorbornene (**5**) was converted to active **6** directly by methoxymercuration–demercuration[9] as follows. To a stirred suspension of 2.91 g (9.12 mmol) of mercuric acetate in 18 ml of methanol was slowly added a solution of 1.55 g (9.12 mmol) of (+)-**5**, $[\alpha]^{25}_{\mathrm{D}}$ 202° ($CHCl_3$), in 5 ml of methanol. The resulting colorless solution was stirred for 10 min at room temperature and then cooled and treated with 9 ml of 3 M sodium hydroxide. To the resulting yellow suspension was added (dropwise) a solution of 0.15 g (3.97 mmol) of sodium borohydride in 9 ml of 3 M sodium hydroxide solution. This gave a grey-black suspension that was stirred for 2 hr to coagulate the mercury. The resulting mixture was extracted with pentane. After drying ($MgSO_4$) the pentane was removed under reduced pressure. The residual liquid ether, 1.84 g (100%), was purified by column chromatography (Florisil with hexane as eluent). This gave (+)-**6**, $[\alpha]^{25}_{\mathrm{D}}$ 46.8° (c 4.10, $CHCl_3$). This corresponds to an absolute rotation of about $[\alpha]^{25}_{\mathrm{D}}$ 73° ($CHCl_3$) for **6**. The nmr spectrum had a singlet at τ 2.91 (4 H), a multiplet at τ 6.75–6.91 (1 H), a methyl singlet at τ 6.75 (3 H), a multiplet at τ 7.61–7.97 (2 H), a doublet (with unresolved fine splitting) at τ 8.32 with $J = 9$ cps (1 H), a methyl singlet at τ 8.60 (3 H), a doublet of doublets centered at τ 8.87 with $J = 12$ and $J = 2.5$ cps (1 H), and a methyl singlet at τ 9.27 (3 H).

Registry No.—(−)-**1**, 35001-30-0; (+)-**1**, 21159-73-9; (−)-**2**, 35001-32-2; (±)-**2**, 34969-22-7; (±)-**3**, 34969-23-8; (±)-**3**, 34969-24-9; (±)-**5**, 35001-33-3; (±)-**5**, 34993-32-3; (−)-**5**, 34969-25-0; (±)-**4**, 34993-33-4; (±)-**4**, 34993-34-5; (±)-**6**, 34969-26-1.

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(10) Prepared from anthranilic acid and cyclopentadiene by the method of L. F. Friedman, F. M. Logullo, and D. M. Smith. We thank Professor Friedman for experimental details prior to publication.

(11) Optically active samples had the same spectral properties as racemic samples.