

oxide and 8,9-indane oxide rapidly rearrange to phenols in aqueous acetamide.^{14,15}

The results presented here demonstrate that **1** can be prepared optically active. In addition, the absolute stereochemistry has been related to the sign of rotation for compounds **1**, **5**, and **6**. Preliminary studies with epoxide hydrase demonstrate that optical activity in **1a** is reflected in the optical activity of **3** obtained by enzymatic hydration, thus providing further evidence that the microsomal formation of **1** from naphthalene⁷⁻⁹ is, in fact, an asymmetric synthesis, which forms (+)-(1*R*,2*S*)-1,2-naphthalene oxide of less than 10% optical purity.

Experimental Section

General.—All compounds synthesized were judged pure by nmr spectra and chromatographic properties as compared to those of the known, optically inactive materials. Glassware used in connection with **1a** was soaked in Na₂CO₃ solutions, washed repeatedly with distilled water, and dried to prevent acid-catalyzed isomerizations. Rotations were measured at 20° with a Perkin-Elmer 141 Polarimeter using a 10-cm cell holding 2 ml of solvent. During studies on racemization of **1a**, small aliquots (5–10 μl) were removed at intervals to measure the ratio of **1a** to naphthol by uv spectroscopy. For the acid-catalyzed reaction, the cell contained 24.2 mg of **1a** and 10 μl of HOAc in 2.0 ml of CH₃OH (data in Figure 1). For the base-catalyzed racemization, the cell contained 12.1 mg of **1a** and 10 mg of KOH in 2.0 ml of CH₃OH. In the later experiment, the rotation decreased 25% in a linear fashion during a 20-hr period.

(–)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**5**).—A cold solution (0°) of (+)-peroxycamphoric acid (30.0 g, 0.148 mol) in 200 ml of CHCl₃ was added dropwise (0.5 hr) to stirred suspension of anhydrous sodium carbonate (8.0 g) and 1,2-dihydronaphthalene (13.6 g, 0.10 mol) in 100 ml CHCl₃ at –28°. The resulting mixture was stored at –20° for 4 weeks, filtered to remove solids, washed with sodium sulfite and sodium carbonate solutions, dried (Na₂SO₄), and concentrated to a small volume. Distillation [bp 55–62° (0.3–0.4 mm)] provided 7.2 g (49%) of **5** with [α]_D²⁰ –6.1°, [α]_D²⁵ –20.1° (c 9, CHCl₃). Lithium aluminum hydride reduction of **5** followed by distillation [67–70° (0.2 mm)] of the product after hydrolysis gave (+)-(2*S*)-2-tetralol¹¹ with [α]_D²⁰ +3.3°, [α]_D²⁵ +11.5° (c 10, CHCl₃), 5% optical purity. Thus, **5** is (–)-(1*S*,2*R*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene with 5% optical purity.

(–)-4-Bromo-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**6**).—N-Bromosuccinimide halogenation of **5** was conducted as previously described (47% yield, mp 94–95°, lit.¹⁰ racemate 94–95°). The resulting product, **6**, was fractionally crystallized from ethyl acetate. The first crop had [α]_D²⁰ –19.0°, [α]_D²⁵ –50.5° (c 10, CHCl₃). Later fractions with lower rotations were discarded. Lithium aluminum hydride reduction of **6** followed by distillation [bp 70° (0.2–0.3 mm)] of the product after hydrolysis gave (+)-(2*S*)-2-tetralol with [α]_D²⁰ +6.7°, [α]_D²⁵ +24.0° (c 10, CHCl₃), 10% optical purity. Thus **6** is (–)-(1*S*,2*R*)-1,2-epoxy-4-bromo-1,2,3,4-tetrahydronaphthalene with 10% optical purity.

(–)-1,2-Naphthalene Oxide (**1a**).—Dehydrohalogenation of **6** was conducted as previously described¹⁰ (75–85% yield), producing **1a** with [α]_D²⁰ –11.7°, [α]_D²⁵ –73.2° (c 2, CHCl₃). Racemization did not occur under the conditions of this reaction, since extending the time for dehydrohalogenation did not decrease the optical activity of the product. The absolute stereochemistry (1*S*,2*R*) and optical purity (10%) are based on **5**. Samples were stored at –80°.

Registry No.—**1a**, 24825-00-1; **5**, 24825-01-2; **6**, 24825-02-3.

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Bridged Polycyclic Compounds. LXIII. Reductive Ring Opening of 3,6-Dibenzotricyclo[3.3.0.0^{2,8}]octadiene¹

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Although the initial report of the formation of a radical anion from cyclopropane³ seems to have been incorrect,^{4,5} considerable interest in substituted cyclopropane radical anions has been generated. Walborsky and Pierce⁶ proposed a cyclopropane radical anion as a transient intermediate in the ring cleavage of 1-methyl-2,2-diphenylcyclopropane by sodium in liquid ammonia. Since they were unable to observe an esr signal, they proposed that the radical anion initially formed suffered rapid ring cleavage and electron-transfer reactions. Miller and Jacoby⁷ found that very rapid cyclopropane ring opening occurred in the reduction of dibenzonorcaradiene with alkali metal in 1,2-dimethoxyethane (DME). Winstein and coworkers⁸ and Katz and Talcott⁹ concluded (from esr data) that the cyclopropane ring was partially broken in the radical anion derived from *cis*-bicyclo[6.1.0]nonatriene; however, there was no evidence for ring opening in the radical anion derived from *trans*-bicyclo[6.1.0]condiene.¹⁰ Papa¹¹ has reported the esr spectrum of the radical anion of 1,2,3-tricyano-1,2,3-tricarboethoxycyclopropane. A series of cyclopropyl-substituted aromatic radical anions^{12,13} and semidiones¹⁴ have been reported, but extensive delocalization of π spin density onto the cyclopropane ring was not observed.

Treatment of a 0.1 *M* solution of 3,6-dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**1**)¹⁵ in dry, deoxygenated DME with freshly cut sodium or potassium metal at 0° yielded a dark red solution within a short time. A similar solution was produced instantaneously when a solution of **1** in DME was treated with a solution of sodium biphenyl or sodium naphthalene radical anion.

It was demonstrated by esr spectroscopy that the red solution was not paramagnetic. Only with concentrated solutions of **1** (>0.1 *M*) in the presence of an excess of sodium-potassium alloy (DME, –40°) was an esr signal detected. The esr signal was very weak

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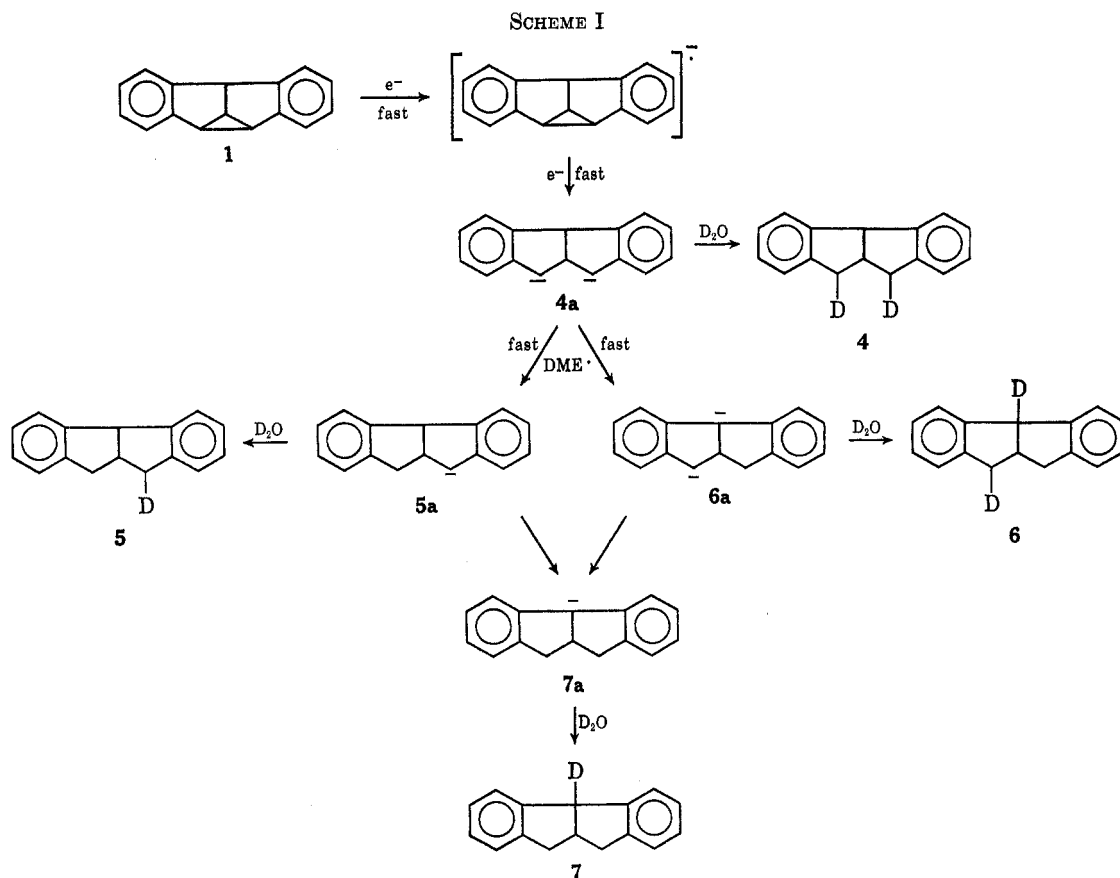
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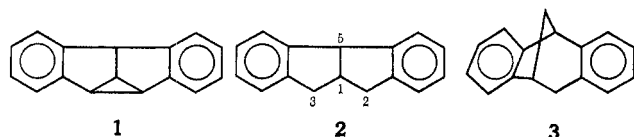
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and could be only partially resolved (total spectrum width was about 23 G), presumably due to line broadening by rapid electron exchange in the concentrated solutions. Numerous attempts to generate the radical anion of 1 by reaction of a solution of 1 with a sodium or potassium mirror in DME or tetrahydrofuran (THF) at -78° (standard high-vacuum techniques)¹⁶ led only to the diamagnetic red solution. When a solution of sodium biphenyl was treated with a fourfold excess of 1 in DME at -78° , only the biphenyl radical anion could be detected by esr. When this latter solution was warmed above -40° , the red diamagnetic solution was produced.

When 1 was treated with sodium biphenyl in DME at 0° and the resulting red solution was quenched with water, the only volatile products were biphenyl, 3,6-dibenzobicyclo[3.3.0]octadiene (2),^{17,18} and 1. No dibenzobicyclo[3.2.1]octadiene (3) was detected. The



ratio of 2:1 was dependent upon the initial ratio of sodium biphenyl to 1. When the molar ratio of sodium biphenyl to 1 was 2:1 or greater, only 2 and biphenyl were observed (*i.e.*, 2 mol of sodium biphenyl convert 1 mol of 1 to 1 mol of 2).

When deuterium oxide was used to quench the reactions of 1 with sodium biphenyl, deuterium was incor-

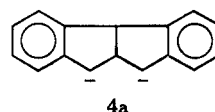
porated at C-2, C-8, and C-5 of 2 (no deuterium was detected in the recovered 1). Typical deuterium incorporation data are shown in Table I. The reductive

TABLE I
DEUTERIUM INCORPORATION IN
DIBENZOBICYCLO[3.3.0]OCTADIENE^a

Reaction time	Observed ratio, 2:1	Deuterium incorporation in 2 ^b	
		C-5	C-2 + C-8
10 sec	0.63	0.1	1.4
30 sec	0.71	0.1	1.4
10 min	0.83	0.2	1.0
2 hr	0.83	1.0	0.0

^a Formed by reaction of equimolar amounts ($\sim 0.1 M$ solutions) of 1 and sodium biphenyl in DME at 0° ; quenching with deuterium oxide. ^b Deuterium analysis by pmr integration (relative to eight aromatic hydrogens).

ring opening of 1 appears to involve the dianion 4a



since quenching with deuterium oxide after very short reaction times gave a large fraction of 2 with two deuterium atoms at C-2 and C-8. When the reactions were quenched with deuterium oxide after longer reaction times, lesser deuterium incorporation was observed at C-2 and C-8, but very significant deuterium incorporation was observed at C-5 (after a 2-hr reaction period, quenching with deuterium oxide gave 2 with two deuterium atoms at C-2 and C-8, but with 1.0 deuterium atom at C-5).

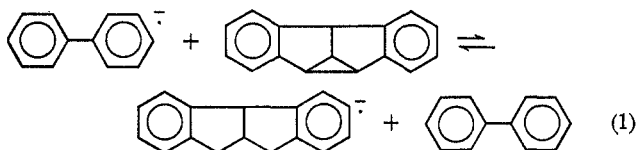
An analysis of the described results leads us to postulate the mechanistic scheme in Scheme I. At 0° , ring

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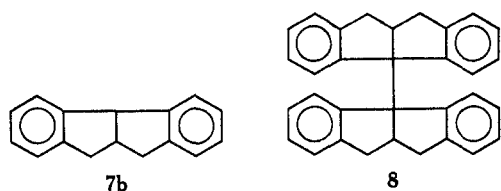
opening and further reduction (or *vice versa*) of the transient radical anion to the dianion **4a** must be extremely facile and irreversible. Thus, in the reaction of sodium biphenyl with **1**, the reaction (eq 1) is driven from left to right by the formation of **4a**. Jagur-



Grodzinski and Szwarc¹⁹ have recently shown in related systems that equilibria, such as eq 1, greatly favor the radical anion of the hydrocarbon with the higher electron affinity. If biphenyl has a significantly higher electron affinity than **1**, the equilibrium (eq 1) should greatly favor biphenyl radical anion and no overall reaction would be observed in the absence of secondary processes (*e.g.*, formation of **4a**). At -78° , the ring opening must be extremely slow and overall electron transfer from sodium biphenyl to **1** cannot be detected. When an alkali metal mirror was used as the reductant, ring opening occurred even at -78° and must have taken place on the metal surface.

The dianion **4a** is very unstable (significant amounts of **4** were formed only if the reaction was quenched after very short reaction times), possibly because of the close proximity of the two negatively charged centers, and reacts very rapidly, either by proton abstraction from the solvent to give **5a** or by rearrangement to **6a**. Both **5a** and **6a** appear to be converted to **7a**, since quenching with deuterium oxide after long reaction times led to **7** as the only dibenzobicyclo[3.3.0]octadiene isolated. That **7a** is not only more stable than **5a**, but also more accessible kinetically, was demonstrated by the reaction of **2** with potassium *t*-butoxide in hexadeuteriodimethyl sulfoxide (DMSO-*d*₆), which gave **7** exclusively.

Oxidation of a solution of **7a** with iodine or molecular oxygen gave **2** and the symmetrical dimer **8**. The



dimer must arise by dimerization of the radical **7b**, a one-electron oxidation product of **7a**.

Experimental Section

General.—3,6-Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**1**) and 3,6-dibenzobicyclo[3.3.0]octadiene (**2**) were prepared by the method of Ciganek.¹⁵ 1,2-Dimethoxyethane (DME) was distilled from sodium-potassium alloy and then from sodium benzophenone ketyl directly into the reaction flask. Sodium biphenyl radical anion was prepared by the method of Liggett.²⁰ Gas-liquid partition chromatographic (glpc) analyses and separations were accomplished with 15% diethylene glycol succinate (DEGS) on Chromosorb W columns.

Reduction of 1 with Sodium Biphenyl.—Dry, prepurified N₂ was bubbled through a solution of 204 mg (1.0 mmol) of **1** in 10 ml of DME in a 25-ml round-bottom flask sealed with a rubber

serum stopper for 2 hr at 0°. The desired volume of a 0.3 M solution of sodium biphenyl in DME was added *via* a syringe. The solution was stirred at 0° for the desired period of time and then 0.3 ml of water (or D₂O) was added *via* a syringe. The solution was added to 100 ml of ether and the ethereal solution was extracted with 30-ml portions of saturated NaHCO₃ and NaCl solutions, dried (MgSO₄), and concentrated *in vacuo*. The pure components, **1** and **2**, were isolated by preparative glpc (7 ft × 3/8 in. column packed with 15% DEGS on Chromosorb W, 175°, helium flow of about 600 cm³/min) and identified by comparison of their retention volumes (10,800 and 16,200 cm³, respectively), pmr spectra,²¹ and melting points^{17,18} with those of the authentic compounds; pmr of **2** (CCl₄) δ 2.6–3.5 (m, 5), 4.6 (d, 1, *J* = 7 Hz), 7.0–7.5 (m, 8).

Base-Catalyzed Hydrogen-Deuterium Exchange of 2.—To a deoxygenated solution of 103 mg (0.50 mmol) of **2** in 2 ml of DMSO-*d*₆ was added 66 mg (0.59 mmol) of freshly sublimed potassium *t*-butoxide. The solution was stirred at 25° for 4 hr and then 1.0 ml of D₂O was added. The mixture was extracted with 100 ml of ether. The ethereal solution was washed several times with water, dried (MgSO₄), and concentrated *in vacuo*. The pure dibenzobicyclo[3.3.0]octadiene was isolated by preparative glpc (same conditions as above). A pmr spectrum of the pure compound showed the complete disappearance of the hydrogen located at δ 4.6 (the hydrogen at C-5 in **2**). No deuterium incorporation at C-2 and C-8 could be detected by pmr.

Oxidation of 7a.—To a solution of **7a** (prepared from 278 mg (1.36 mmol) of **1** and 2.80 mmol of sodium biphenyl) in 15 ml of DME was added 169 mg (0.67 mmol) of iodine in 5 ml of DME. The solution was stirred at 0° for 20 min and then added to 100 ml of ether. The ethereal solution was extracted with saturated NaHCO₃, 10% Na₂S₂O₃, and saturated NaCl solutions, dried (MgSO₄), and concentrated *in vacuo*. The crude product mixture was passed over 40 g of Merck 71707 alumina. Elution with petroleum ether (bp 60–70°) yielded a mixture of **2**, biphenyl, and **8**. Recrystallization of this mixture from methanol gave 84 mg (0.21 mmol, 31%) of **8**: mp 233–235°; pmr (CDCl₃) δ 2.3–3.3 (m, 10), 6.8–7.4 (m, 16); mass spectrum *m/e* 205 was the major peak (one-half of that expected for the molecular ion).

Anal. Calcd for C₃₂H₂₈: C, 93.66; H, 6.34. Found: C, 93.50; H, 6.45.

Registry No.—**1**, 2199-28-2; **8**, 25244-21-7.

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Condensation between Homophthalic Acid and *o*-Chlorobenzaldehydes

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The reaction between homophthalic acid and aromatic aldehydes in the presence of an organic base leads to 4-arylidenehomophthalic anhydrides.¹ During studies of this reaction in these laboratories homophthalic acid and *o*-chlorobenzaldehyde (at 240–250°) in the presence of piperidine unexpectedly gave 2-(2-hydroxyphenyl)indenone-3-carboxylic acid lactone (**2**). Similarly, 2,6-dichlorobenzaldehyde and 2,4-dichlorobenzaldehyde gave **3** and **4**, respectively. Compounds **2**, **3**, and **4** are red crystalline substances subliming at 250–300° (1 atm).

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