sulting mixture was heated at 120° under reflux until carbon dioxide evolution ceased, cooled, and filtered, and the filtrate was analyzed for ester and alkyl iodide. Using acetic anhydride, the following percentage yields were obtained per atom of iodine: ZnI_2, 16, 21; SnI_4, 87, 67; using butyric anhydride, PbI_2, 58, 24.

Mercuric iodide gave ester but very little or no alkyl iodide when employed in the above process. The precipitate formed upon ozonization of mercuric iodide in excess propionic anhydride was isolated by suction filtration, washed several times with carbon tetrachloride, and dried.

Anal. Calcd for $Hg(IO_3)_2$: Hg, 36.44; I, 46.12. Found: Hg, 36.28; I, 46.12.

Reaction of Propionic Anhydride with Mercuric Iodate.—In a flask equipped with a Dry Ice–acetone reflux condenser, a nitrogen inlet tube with a stopcock, and a magnetic stirring bar, were placed 0.050 mol of propionic anhydride and 0.0050 mol of mercuric iodate. A weighed Ascarite trap for carbon dioxide absorption was attached to the reflux condenser. A wet-test meter was attached to the Ascarite trap. Air was swept from the system by a stream of nitrogen. The stirred solution was heated until gas evolution ceased (0.0170 mol evolved), cooled to room temperature, and the wet-test meter was disconnected. The reaction flask was immersed in a Dry Ice–acetone bath, the nitrogen inlet tube stopcock was opened, and the residual gaseous product was swept through the Ascarite trap. Carbon dioxide, 0.0099 mol (99% yield), was found. The difference between total gas evolution, as measured by the wet-test meter, and carbon dioxide evolution, as measured by the Ascarite trap, was 0.0071 mol, a 72% yield of oxygen (identified by mass spectrometry). Quantitative vpc analysis of the liquid reaction mixture showed ethyl propionate, 0.0094 mol (yield 87% based on propionic anhydride), to be present. The reaction mixture was filtered and the filtrate was titrated to a phenolphthalein end point with standardized sodium hydroxide. Unreacted propionic anhydride, determined as propionic acid, 0.039 mol, was found. Air drying of the filtered solid yielded 0.0047 mol (94% yield) of mercuric iodide.

Reaction of Valeric Anhydride with Mercuric Oxide and Iodine.—In a flask equipped with a condenser, a pressure-equalizing dropping funnel, a thermometer, and a magnetic stirring bar, were placed 15 ml of 1,2-dibromoethane, 0.050 mol of valeric anhydride, and 0.050 mol of red mercuric oxide. A solution of 0.050 mol of iodine dissolved in 71 ml of 1,2-dibromoethane was place in the dropping funnel. The slurry of valeric anhydride and mercuric oxide was heated with stirring, and the solution of iodine in 1,2-dibromoethane was slowly added. A temperature of 100° was required to decolorize the iodine. Gas evolution accompanied the decolorization. At the end of the iodine addition, gas evolution ceased and a clear solution containing red mercuric iodide was obtained. Vpc analysis revealed the presence of 0.025 mol of butyl valerate. Based upon iodine, the yield is 50%. Butyl iodide was not present.
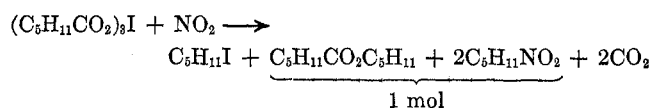
Decomposition of Iodine Tricaproate in the Presence of Mercuric Oxide.—A mixture of 0.025 mol of caproic anhydride and 0.0025 mol of iodine was ozonized, red mercuric oxide, 0.0026 mol, was added, and the stirred solution was heated. At 120° a sudden and vigorous evolution of gas occurred, accompanied by the appearance of free iodine throughout the solution. Within 60 sec, gas evolution ceased and the free iodine color disappeared. Yellow mercuric iodide soon precipitated from the colorless solution; upon cooling, the red crystalline modification was formed. Carbon dioxide, 0.0074 mol, was evolved. Vpc analysis revealed the presence of 0.0068 mol (91% yield) of amyl caproate.

The above procedure, with only minor modification, was employed for all the liquid anhydrides studied. In the case of the solid stearic anhydride, stoichiometric amounts of anhydride and iodine were employed in the solvent 1,2,3-trichloropropane, and the mercuric iodide was separated from the heptadecyl stearate by thorough washing with aqueous KI.

When mercuric oxide was replaced by lead(II) oxide in the above reaction, alkyl iodide but no ester was formed. With red lead (Pb_3O_4), both ester (36% yield) and alkyl iodide were obtained.

Decomposition of Iodine Tricaproate in the Presence of Excess Nitrogen Dioxide.—A suspension of iodine tricaproate in caproic anhydride was prepared as described immediately above. The ozone inlet tube was replaced with a nitrogen dioxide inlet tube, and excess nitrogen dioxide was passed into the solution. The solution was heated with stirring and maintained at 130–135° for

30 min. The solution was cooled to room temperature and analyzed by vpc. Amyl iodide, 0.0041 mol (82% yield), amyl caproate, 0.0014 mol (28% yield), and 1-nitropentane, 0.0050 mol (25% yield), were obtained. Yields are based on the following equation.

$$(C_5H_{11}CO_2)_3I + NO_2 \longrightarrow$$

$$C_5H_{11}I + \underbrace{C_5H_{11}CO_2C_5H_{11} + 2C_5H_{11}NO_2 + 2CO_2}_{1\ mol}$$

Reaction of Mercuric Iodate and Propionic Anhydride with Active Methylene Compounds.—A mixture of 0.010 mol each of propionic anhydride and cyclohexanone and 0.0035 mol of mercuric iodate was maintained at 135–140° under reflux for 12 hr. Upon cooling, a light wine-colored solution containing red mercuric iodide was obtained. Vpc analysis of the solution revealed ethyl propionate to be absent. The only major reaction products were α-propionoxycyclohexanone, 0.0022 mol (31% yield), and propionic acid.

Replacement of cyclohexanone with cyclohexene under the same reaction conditions afforded 0.0017 mol (24% yield) of 2-cyclohexenyl propionate and propionic acid as the only major reaction products.

Replacement of cyclohexanone with 1-octene produced 0.0015 mol (21% yield) of 1-octen-3-yl propionate, 0.0020 mol (29% yield) of *trans*-2-octenyl propionate, and propionic acid as the only major reaction products. These products were identified by ir, nmr, and mass spectra determined on samples isolated by vpc.

Optically Active 1,2-Naphthalene Oxide

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Valence tautomerism in unsaturated medium ring systems is an area of considerable current interest.[2] Certain arene oxides (benzene oxide,[3] 3,4-toluene oxide[4]) exist as equilibrium mixtures of oxide and oxepin forms, while others appear to exist solely in either the oxide (8,9-indan and 9,10-tetralin oxide)[5] or the oxepin form (1,2-dimethyl-1,2-benzene oxide[6]). Spectroscopic studies on 1,2-naphthalene oxide (1) suggest that it exists solely in the oxide form but do not exclude the possibility of an equilibrium between 1 and 2 which greatly favors 1. If such an equilibrium does not exist or if it exists and the interconversion rate is slow, 1

(1) Fellow in the Visiting Program of the U. S. Public Health Service, 1968–1969, on leave of absence from Queen's University, Belfast, N. Ireland.

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should be isolable in optically active forms. Discrete optical enantiomers of **1** were indeed inferred from the microsomal metabolism of **1** and naphthalene. Monooxygenases oxidize napthalene to **1** which is rapidly converted to (−)-*trans*-1,2-dihydroxy-1,2-dihydronaphthalene (**3**) by a stereospecific epoxide hydrase.[7-9]

1 ⇌ (?) **2**

3
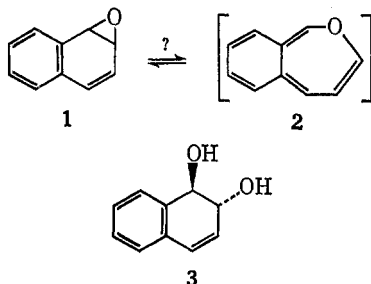
The optical activity associated with **3** is ~10% lower when racemic **1** is employed in place of enzymatically generated **1** from naphthalene as the substrate for the epoxide hydrase. This suggests an asymmetric synthesis of an arene oxide by microsomal monooxygenases. Testing this hypothesis directly is not practical since enzymatically synthesized **1** is not accessible in sufficient quantity.[9]

The route to optically active **1** followed the original synthesis of racemic material[10] with the exception that optically active 1,2-dihydronaphthalene oxide (**5**) was used. The latter was prepared by (+)-peroxycamphoric acid (PCA) oxidation of 1,2-dihydronaphthalene (**4**). Bromination with N-bromosuccinimide (NBS)

4
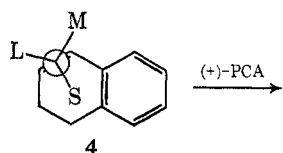
L, M, S refer to
groups in (+)-PCA
of decreasing size

5 → (LiAlH₄) → **7**

5 → (NBS) → **1a** ← (−HBr) ← **6**

6 → (LiAlH₄) → **7**
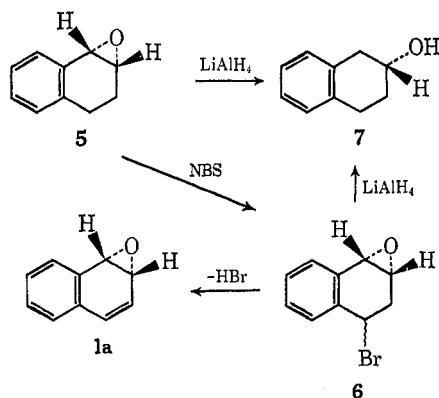
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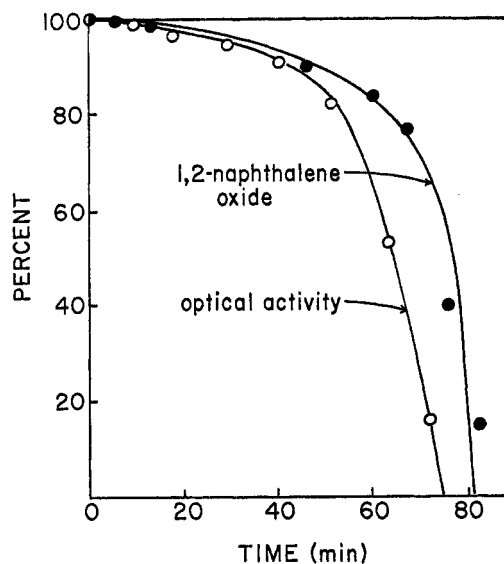(10) E. Vogel and F. G. Klärner, *Angew. Chem., Int. Ed. Engl.*, **7**, 734 (1968).

Figure 1.—Per cent remaining optical activity (O) and 1,2-naphthalene oxide (●) with time in the presence of acetic acid.

yielded (−)-1-bromo-1,2-dihydronaphthalene-3,4-oxide (**6**). Reduction of **5** and **6** with LiAlH₄ provided (+)-(2*S*)-2-tetralol (**7**)[11] of 5 and 10% optical purity, respectively. The increased optical purity of **6** relative to **5** was the result of fractional crystallization. The major optical antipode produced in the (+)-PCA oxidation is consistent with that predicted from consideration of the lowest energy transition state for the reaction[12] (see **4**). Dehydrohalogenation[9] of **6** produces optically active **1a** in high yield (85%). The optical purity of **1a** was assumed to be ~10%. Optical rotatory dispersion on **1a** and **5** show simple negative plain curves above 285 and 240 mμ, respectively.

Measuring the optical stability of **1a** is complicated by the chemical instability of the compound. Naphthalene oxide readily isomerizes to naphthol in the presence of heat or weak acids such as naphthol. Thermal isomerization such as that studied for carbocyclic systems[13] could not be attempted because of the rapid isomerization of **1a** to naphthol in methanol at 50°. However, **1a** is both optically and chemically stable at −80°. Initial experiments showed complete chemical and optical stability for 24 hr in CHCl₃ and 8 hr in CH₃OH at 20°. Addition of a trace of acetic acid to methanolic solution of **1a** caused complete loss of optical activity within 1.5 hr (Figure 1) along with a parallel formation of naphthol. The data (Figure 1) suggest that loss of optical activity proceeds at a slightly greater rate than naphthol formation. This is particularly true during the naphthol-catalyzed portion of the reaction and thus may indicate some racemization. Addition of a small amount of methanolic KOH to a CH₃OH solution of **1a** causes racemization without isomerization to naphthol or formation of other products (see Experimental Section). Methanolic acetamide caused neither racemization nor isomerization over a period of several hours, which was surprising, since benzene

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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 naphthalene[7-9] is, in fact, an asymmetric synthesis, which forms (+)-(1R,2S)-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 Na_2CO_3 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 CH_3OH (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 CH_3OH. 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 $CHCl_3$ 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 $CHCl_3$ 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 (Na_2SO_4), and concentrated to a small volume. Distillation [bp 55–62° (0.3–0.4 mm)] provided 7.2 g (49%) of 5 with $[\alpha]_{589}$ −6.1°, $[\alpha]_{365}$ −20.1° (c 9, $CHCl_3$). Lithium aluminum hydride reduction of 5 followed by distillation [67–70° (0.2 mm)] of the product after hydrolysis gave (+)-(2S)-2-tetralol[11] with $[\alpha]_{589}$ +3.3°, $[\alpha]_{365}$ +11.5° (c 10, $CHCl_3$), 5% optical purity. Thus, 5 is (−)-(1S,2R)-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 $[\alpha]_{589}$ −19.0°, $[\alpha]_{436}$ −50.5° (c 10, $CHCl_3$). 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 (+)-(2S)-2-tetralol with $[\alpha]_{589}$ +6.7°, $[\alpha]_{365}$ +24.0° (c 10, $CHCl_3$), 10% optical purity. Thus 6 is (−)-(1S,2R)-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 described[10] (75–85% yield), producing 1a with $[\alpha]_{589}$ −11.7°, $[\alpha]_{365}$ −73.2° (c 2, $CHCl_3$). 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 (1S,2R) 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}]octadiene[1]

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Although the initial report of the formation of a radical anion from cyclopropane[3] seems to have been incorrect,[4,5] considerable interest in substituted cyclopropane radical anions has been generated. Walborsky and Pierce[6] 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 Jacoby[7] found that very rapid cyclopropane ring opening occurred in the reduction of dibenzonorcaradiene with alkali metal in 1,2-dimethoxyethane (DME). Winstein and coworkers[8] and Katz and Talcott[9] 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] Papa[11] has reported the esr spectrum of the radical anion of 1,2,3-tricyano-1,2,3-tricarboethoxy-cyclopropane. A series of cyclopropyl-substituted aromatic radical anions[12,13] and semidiones[14] 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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