2-(α-Hydroxyisopropyl)-5-methylcyclohexanol.—To a filtered ethereal solution of methyllithium prepared from 9.24 g. (1.32 g.-atoms) of lithium and 93.7 g. (0.66 mole) of methyl iodide was added dropwise a solution of 23.2 g. (0.135 mole) of methyl 2-hydroxy-4-methylcyclohexanecarboxylate in 50 ml. of anhydrous ether. The mixture was stirred for 22 hr. and decomposed by dropwise addition of 150 ml. of water. The layers were separated and the aqueous phase was extracted repeatedly with ether. The combined ether layers were dried and distillation gave 16.9 g. (72.8%) of a viscous, colorless oil, b.p. 107–110° (0.85 mm.), $n^{20}\mathrm{D}$ 1.4725, $\nu_{\max}$ 3.0 μ [for 2-(α-hydroxyisopropyl)-5-methylcyclohexanol, lit.[11] b.p. 102–106° (0.3–0.6 mm.)].

2-(α-Hydroxyisopropyl)-5-methylcyclohexanone.—To a cooled and stirred solution of 7.56 g. (0.044 mole) of 2-(α-hydroxyisopropyl)-5-methylcyclohexanol in 70 ml. of pure acetone was added dropwise 11.0 ml. of chromic oxide in sulfuric acid–water.[7] After stirring for 30 min. isopropyl alcohol was added to destroy the excess oxidant. The mixture was filtered and the filtrate was taken up in ether and washed with water. The pale yellow ether solution was dried and distilled to give 5.17 g. (69.2%) of a colorless liquid: b.p. 93–95° (10 mm.); $n^{19}\mathrm{D}$ 1.4646; $\nu_{\max}$ 2.86 and 5.95 μ; n.m.r. signals at 0.89, 1.10, 1.16, 1.66–2.58 (broad), and 3.37 p.p.m.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.76; H, 10.53.

(±)-Pulegone.—A mixture of 3.99 g. of 2-(α-hydroxyisopropyl)-5-methylcyclohexanone and a few small crystals of iodine was distilled under diminished pressure to yield 2.92 g. (81.8%) of a colorless oil with characteristic peppermint odor: b.p. 78–80° (7 mm.); $n^{16}\mathrm{D}$ 1.4856; $\lambda^{\text{alc}}_{\max}$ 253.5 mμ (log ϵ 3.86); n.m.r. signals at 0.95, 1.04, 1.75, 1.92, and 2.05–2.92 (broad) p.p.m. [for (±)-pulegone: lit. b.p. 220–222°, $n^{18}\mathrm{D}$ 1.4846[4]; b.p. 101–103° (10 mm.), $n^{20}\mathrm{D}$ 1.4845[5]; and b.p. 95–96° (11 mm.), $n^{20}\mathrm{D}$ 1.4869[8]]. The infrared spectrum of (±)-pulegone was identical with that of a sample of (+)-pulegone isolated by v.p.c.

The 2,4-dinitrophenylhydrazone of (±)-pulegone melted at 145–147° after recrystallization from methanol, while the 2,4-dinitrophenylhydrazone of (+)-pulegone melted at 150–151° after recrystallization from ethanol [for (±)-pulegone 2,4-DNP: lit. m.p. 148,[4] 142,[5] and 148–149°[8]].

The oxidation of 15.7 g. of 2-(α-hydroxyisopropyl)-5-methylcyclohexanol and then direct distillation of the hydroxy ketone from a trace of iodine gave 8.21 g. (59.1%) of (±)-pulegone, b.p. 62–63° (1.1 mm.).

Methyl 2-Hydroxycyclohexanecarboxylate.—Methyl salicylate (180 g., 1.18 moles) was hydrogenated at 1600 p.s.i. and 150° using W-2 Raney nickel catalyst. The catalyst was removed and distillation gave 41.9 g. of saturated ester, b.p. 84–88° (2 mm.), $n^{21}\mathrm{D}$ 1.4640 [lit.[11] b.p. 106–110° (13 mm.)], and *ca.* 150 ml. of nondistillable polyester. The polyester was dissolved in 200 ml. of methanol containing 2.0 g. of *p*-toluenesulfonic acid and the solution was heated at reflux for 24 hr. Distillation yielded an additional 97.7 g. of the saturated ester, b.p. 85–88° (2 mm.), $n^{22}\mathrm{D}$ 1.4641.

2-(α-Hydroxyisopropyl)cyclohexanol.—The reaction of methyllithium, prepared from 21.0 g. (3 g.-atoms) of lithium and 213 g. (1.5 moles) of methyl iodide, with 34.1 g. (0.216 mole) of methyl 2-hydroxycyclohexanecarboxylate produced 22.3 g. (65.4%) of a viscous oil, b.p. 100–102° (0.55 mm.), $n^{23}\mathrm{D}$ 1.4760 [lit.[11] b.p. 86–88° (18 mm.)].

2-(α-Hydroxyisopropyl)cyclohexanone.—2-(α-Hydroxyisopropyl)cyclohexanol (22.3 g.) was oxidized according to the Jones procedure[7] described above to give 12.2 g. (54.5%) of a colorless oil: b.p. 78–80° (4 mm.); $n^{20}\mathrm{D}$ 1.4684; $\nu_{\max}$ 2.85 and 5.90 μ; n.m.r. signals at 1.13, 1.20–2.50 (broad), and 3.42 p.p.m.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.38; H, 10.36.

An attempt to purify the hydroxy ketone by v.p.c. gave two main peaks which were identified as cyclohexanone and acetone by their infrared spectra.

2-Isoproppylidencyclohexanone.—2-(α-Hydroxyisopropyl)cyclohexanone (7.76 g.) containing a trace of iodine, was distilled to yield 4.74 g. (69.1%) of a colorless liquid with a characteristic peppermint odor: b.p. 62–63° (3.5 mm.); $n^{20}\mathrm{D}$ 1.4921; $\nu_{\max}$ 5.97 and 6.22 μ; $\lambda_{\max}$ 253 mμ (log ϵ 3.87; n.m.r. signals at 1.78, 1.92, 1.96, and 2.0–2.67 p.p.m. [for 2-isopropylidenecyclohexanone: lit. b.p. 120–125° (20 mm.), $n^{20}\mathrm{D}$ 1.4919[5]; b.p. 103.5–104.5° (24 mm.), $n^{20}\mathrm{D}$ 1.4922, $\lambda_{\max}$ 254 mμ (log ϵ 3.80)[6]].

The oxidation of 9.64 g. of 2-(α-hydroxyisopropyl)cyclohexanol and direct distillation of the intermediate hydroxy ketone with iodine gave 3.85 g. (45.8%) of 2-isopropylidenecyclohexanone.

The 2,4-dinitrophenylhydrazone (2,4-DNP) derivative of 2-isopropylidenecyclohexanone crystallized as crimson plates from ethanol–chloroform, m.p. 177–178.5° [for 2-isopropylidenecyclohexanone 2,4-DNP: lit. m.p. 182–183,[6] 162–163,[5] and 181.5–182.5°[12]].

Methyl 2-Hydroxy-5-methylcyclohexanecarboxylate.—A mixture of 88 g. (0.53 mole) of methyl 2,5-cresotate, b.p. 68° (0.55 mm.), $n^{18}\mathrm{D}$ 1.5325, 12 g. of nickel boride P-1 catalyst,[13] and 25 ml. of ethanol was shaken at 150° under 1800 p.s.i. of hydrogen for 24 hr. A fresh batch of catalyst was added and the hydrogenation was allowed to continue for an additional 24 hr. Distillation afforded 70.7 g. of a colorless liquid, b.p. 57–63° (0.3 mm.), $n^{18}\mathrm{D}$ 1.4725. Analysis by n.m.r. indicated that the saturated ester was contaminated by *ca.* 20% of the original aromatic ester.

2-(α-Hydroxyisopropyl)-4-methylcyclohexanol was obtained by the reaction of methyllithium with 2-hydroxy-5-methylcyclohexanecarboxylate and exhibited b.p. 100–106° (0.65 mm.), $n^{18}\mathrm{D}$ 1.4732.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.79; H, 11.63. Found: C, 69.97; H, 11.85.

2-Isopropylidene-4-methylcyclohexanone.—Oxidation of 1.4 g. of 2-(α-hydroxyisopropyl)-4-methylcyclohexanol according to the Jones procedure[7] afforded, after distillation from a trace of iodine, 0.4 g. (47%) of a colorless liquid, b.p. 70–71° (1.2 mm.), $n^{12}\mathrm{D}$ 1.4887, $\lambda_{\max}$ 250 mμ (log ϵ 3.85).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.95; H, 10.53. Found: C, 78.69; H, 10.60.

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[12] R. T. Conley and B. E. Nowak, *J. Org. Chem.*, **27**, 3196 (1962).

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The Preparation of $\Delta^{9,10}$-Octalin-2,7-dione

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As a result of other investigations we have prepared $\Delta^{9,10}$-octalin-2,7-dione (**3**) and $\Delta^{1,9}$-octalin-2,7-dione (**4**), depicted in its enolic form, *via* the Birch reduction of 2,7-dimethoxynaphthalene (**1**). The usefulness of **3** as an intermediate in the synthesis of other compounds, particularly in the terpene and steroid fields, together with the recent interest[1,2] in the reduction of **1** with alkali metals in liquid ammonia, prompts us to report our results.

Weinstein and Fenselau,[1] in an attempt to obtain **2**, reduced **1** with lithium in ammonia and found only the hydrogenolysis products 6-methoxy-1,2,3,4-tetrahydronaphthalene and 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene. Marshall and Anderson[2] were successful in obtaining **2** from **1** but required a minimum eightfold excess of lithium or potassium in ammonia–ether–ethanol in order to effect the reduction.

We have found that **1** is easily reduced to **2** in 96% yield with sodium (40% excess) in ammonia–tetrahydrofuran–ethanol.[3] This procedure is the simplest route to **2** commensurate with low reducing agent–

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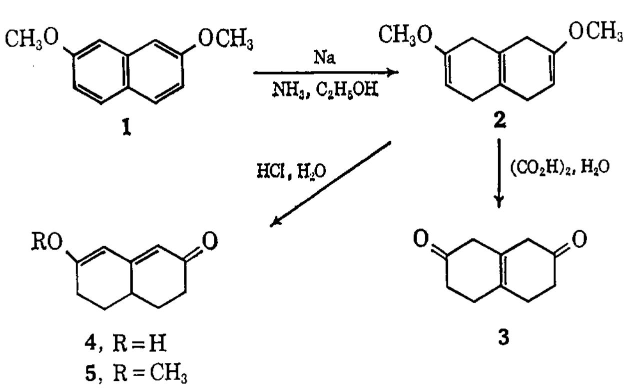
[1] B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **29**, 2102 (1964).

[2] J. A. Marshall and N. H. Anderson, *ibid.*, **30**, 1292 (1965).

[3] The reduction goes equally well with ether in place of the tetrahydrofuran, but **1** is much more soluble in the latter solvent.



substrate ratio and high yield. Its success is realized only by recognizing the importance of using distilled ammonia as the solvent.[4]

Hydrolysis of **2** with aqueous methanolic oxalic acid at room temperature produces **3** in 79% yield. The infrared spectrum of **3** displays only one band in the carbonyl stretching region at 5.84 μ, normal for unconjugated cyclohexanones. The n.m.r. spectrum of **3** confirms its structure by displaying singlets at τ 7.21 and 7.48 with relative intensities of 1:2, respectively.

The preparation of **4** is most easily accomplished by hydrolyzing **2** with hot 1 *N* hydrochloric acid. When the reaction is cooled, **4** precipitates and is readily isolated by filtration in 70% yield. The ease of O alkylation of **4** is illustrated by the fact that warming it in methanol in the presence of a few drops of concentrated hydrochloric acid results in an 80% yield of **5**.

The reactions of **3** and **4** are currently under study in order to determine their usefulness as intermediates in organic syntheses.

Experimental

2,7-Dimethoxy-1,4,5,8-tetrahydronaphthalene (**2**).—Liquid ammonia (1250 ml.) was collected in a suitable round-bottom flask, cooled to −78°, by passing the gas from a cylinder through a gas-washing tower containing solid potassium hydroxide. To the ammonia was added a solution of 2,7-dimethoxynaphthalene[1] (45.0 g., 0.24 mole) dissolved in tetrahydrofuran (200 ml.) and ethanol (150 ml.). To this stirring mixture, cooled to −78°, sodium (30.0 g., 1.3 g.-atoms) was added in small pieces over a period of 1 hr. The cooling bath was removed and the ammonia was allowed to evaporate. To the white solid mass that remained ethanol (200 ml.) was added, followed by water (2.5 l.). The crystalline product was filtered off to yield **2**, 44 g. (96%), m.p. 50–54°. Recrystallization of a small sample from methanol afforded an analytical sample, m.p. 67–68°. The infrared and n.m.r. spectra of **2** were in complete agreement with those reported.[2]

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.88; H, 8.32.

$\Delta^{9,10}$-Octalin-2,7-dione (**3**).—To a solution of **2** (0.194 g., 0.001 mole) in methanol (10 ml.) was added 1 *M* aqueous oxalic acid (3.5 ml.) and the mixture was stirred at room temperature for 1 hr. Solid sodium bicarbonate was added to neutralize the mixture and most of the methanol was removed by evaporation at reduced pressure. Water (5 ml.) was added and the mixture was extracted with methylene chloride (three 5-ml. portions). The extracts were combined, dried over magnesium sulfate, filtered, and concentrated to a low-melting solid, 146 mg. This material was recrystallized from hexane to give **3**, 132 mg. (79%), m.p. 59.5–60.5°. The infrared spectrum of **3** in $CHCl_3$ displayed bands at 5.84 (C=O) and 6.2 μ (C=C). The n.m.r. spectrum of **3** in CCl_4 has peaks at τ 7.22 and 7.48 with relative intensities of 1:2, respectively.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.12; H, 7.32.

$\Delta^{1,9}$-Octalin-2,7-dione (**4**).—To 1 *N* hydrochloric acid (300 ml.) was added **2** (19.4 g., 0.1 mole) and the mixture was warmed to 80° with stirring for 1 hr. Upon cooling the reddish solution in ice, a precipitate resulted which was filtered off to give **4**, 11.5 g. (70%), m.p. 172–176°. Recrystallization from ethyl acetate gave a sample with m.p. 178–181°. This material showed spectral properties in ethanol and chloroform identical with those reported.[2]

7-Methoxy-4,4a,5,6-tetrahydro-2(3H)-naphthalenone (**5**).—A solution of enol **4** (0.332 g., 0.002 mole) in methanol (10 ml.) was treated with 2 drops of concentrated hydrochloric acid and warmed on the steam bath for 15 min. The mixture was neutralized with saturated sodium bicarbonate and extracted with methylene chloride (three 10-ml. portions). The combined extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated under vacuum to give **5**, 0.358 g. (99%), m.p. 87–90°. Recrystallization of the sample from hexane afforded an analytical sample with m.p. 93–94°. The infrared spectrum of the sample was identical with that reported.[2] The n.m.r. spectrum of **5** was as follows: singlets at τ 4.30 and 4.59 (two C=C—H), singlet at τ 6.31 ($O-CH_3$), and a multiplet of nine protons at τ 7.4–8.5.

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[4] An elegant investigation of the Birch reduction by Dryden[5] has shown the necessity of using distilled ammonia for this reaction. The presence of as little as 1 p.p.m. of iron in the reaction mixture has greatly altered the course of the reaction.

[5] H. L. Dryden, Jr., G. M. Weber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

Reduction of 2,7-Dimethoxynaphthalene

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In a previous investigation of the Birch reduction of naphthalenic diethers, we reported that treatment of 2,7-dimethoxynaphthalene (I) with lithium metal in liquid ammonia in the initial absence of alcohol gave two hydrogenolysis products. These compounds were identified as 6-methoxytetralin (II) and 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene (III).[1] The expected 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene (IV) was not observed in the reaction mixture. Alternatively, by following a related procedure for the reduction of 2,6-dimethoxynaphthalene,[2] which employed sodium metal in liquid ammonia in the presence of ethanol and the use of tetrahydrofuran as a cosolvent, we now find 2,7-dimethoxynaphthalene to be easily convertible into the desired bisenol ether (IV). This assignment of structure was confirmed by the absence of an intense maximum in the ultraviolet spectrum and by elemental analysis. The compound is apparently unstable; storage in the freezer at −20° under nitrogen retards the discoloration of the material, but after several days the sample is visibly yellow.

Mild hydrolysis by oxalic acid[3] in aqueous methanol at room temperature cleaved the diether IV and formed the even less stable $\Delta^{9,10}$-octalin-2,7-dione (V). The infrared spectrum of the unconjugated ketone exhibited

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