jected to a hydrogen atmosphere, the effect upon the reduction of resorcinol was inconclusive. Although only 1 equiv. of hydrogen was absorbed, no diketone could be isolated from the oily mixture of products.

Attempts to produce 1,4-cyclohexanedione similarly by reduction of hydroquonine failed, although good yields of 1,4-cyclohexanediol were obtained.

Experimental[5]

1,3-Cyclohexanedione.—A solution of resorcinol (11.0 g.) in sodium hydroxide solution (4.8 g. of sodium hydroxide in 20 ml. of water) was hydrogenated in the presence of 1.1 g. of 5% rhodium-on-alumina for 16–18 hr. at 50 p.s.i. in a Parr apparatus. The reduction ceased after the absorption of 1 equiv. of hydrogen. The catalyst was removed by filtration and the aqueous solution was carefully acidified with concentrated hydrochloric acid at 0°. The crude product, 9.1 g. (m.p. 104–106°), was recrystallized from benzene to yield pure 1,3-cyclohexanedione, m.p. 105–107°.

Reduction of Resorcinol to *cis*- and *trans*-1,3-Cyclohexanediol.—A solution of 11.0 g. of resorcinol in ethanol or acetic acid (50 ml.) was hydrogenated in the presence of 1.1 g. of rhodium on alumina at 52 p.s.i. for 2.6 hr. The system absorbed 3 equiv. of hydrogen. After removal of the catalyst and evaporation of the solvent, a viscous oil remained which showed strong -OH absorption in the infrared. The yield of the mixture of diols was 11.1 g.

Reduction of Hydroquinone to *cis*- and *trans*-1,4-Cyclohexanediol. A.—A solution of hydroquinone (11.0 g.) in aqueous alkali (as above) was hydrogenated using 1.1 g. of rhodium catalyst. After 24 hr. the catalyst was removed and the aqueous solution was acidified to yield 6.0 g. of starting material.

B.—When the same amount of hydroquinone and rhodium catalyst was hydrogenated in ethanol or acetic acid solvent, a rapid absorption of 3 equiv. of hydrogen was observed. Removal of the catalyst and evaporation of the solvent yielded 11.7 g. of a viscous oil showing the -OH stretching frequency of the isomeric 1,4-diols, and the absence of any carbonyl absorption.

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(5) Melting points were determined on a Fisher-Johns apparatus and are corrected.

Synthesis of 2-Isopropylidenecyclohexanones. (±)-Pulegone

JOSEPH WOLINSKY, MICHAEL SENYEK, AND STUART COHEN

Department of Chemistry, Purdue University, Lafayette, Indiana

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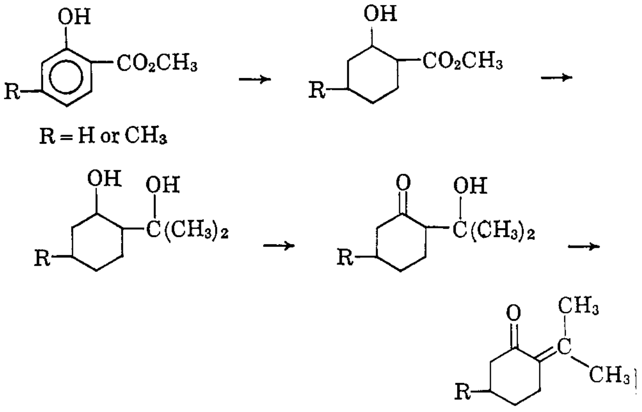
Samples of 2-isopropylidenecyclohexanones, particularly (±)-pulegone, were desired in connection with other investigations being conducted in this laboratory.[1,2] (±)-Pulegone has been prepared by cyclization of citronellic acid[3] and by hydrolysis of the product derived from the reaction of methylmagnesium iodide with the ethylene ketal of 2-carboethoxy-5-methylcyclohexanone.[4,5] 2-Isopropylidenecyclohexanone can also be obtained from the ethylene ketal of 2-carboethoxycyclohexanone, but is only a minor product in the cyclization of 7-methyloct-6-enoic acid.[6] The lack of a general synthetic method and the relative unavailability of certain of the above-mentioned starting materials prompted us to devise a convenient synthesis of 2-isopropylidenecyclohexanones from commercially available salicylic or cresotic acids as outlined below.



Catalytic hydrogenation of methyl 2-hydroxy-4-methylbenzoate using Raney nickel catalyst afforded a mixture of isomeric methyl 2-hydroxy-5-methylcyclohexanecarboxylates. This isomeric mixture was converted into the corresponding mixture of glycols with methyllithium. Oxidation of the glycols according to the Jones procedure[7] gave 2-(α-hydroxyisopropyl)-5-methylcyclohexanone which was converted into (±)-pulegone by distillation from a trace of iodine.

2-Isopropylidenecyclohexanone and 2-isopropylidene-4-methylcyclohexanone were prepared in a similar manner from methyl salicylate and methyl 2-hydroxy-5-methylbenzoate, respectively. It is seen that this procedure is general for the synthesis of substituted 2-isopropylidenecyclohexanones from available salicylic acid derivatives.

Experimental[8]

Methyl 2-Hydroxy-4-methylbenzoate.—A solution of 120 g. (0.789 mole) of 2,4-cresotic acid in 600 ml. of methanol and 10 ml. of concentrated sulfuric acid was heated at reflux for 184 hr. The dark orange mixture was poured into 800 ml. of water and the layers were separated. The aqueous phase was extracted with ether. The combined ether extracts and organic layer were dried and then distilled to give 116.3 g. (88.8%) of a colorless liquid, b.p. 75–76° (1.5 mm.), $n^{18}\mathrm{D}$ 1.5360 (lit.[9] b.p. 242–244°, $n^{15}\mathrm{D}$ 1.5378).

Methyl 2-Hydroxy-4-methylcyclohexanecarboxylate.—A mixture of 102.3 g. (0.616 mole) of methyl 2-hydroxy-4-methylbenzoate, 12 g. of W-2 Raney nickel,[10] and 25 ml. of methanol was stirred for 4 days in a 250-ml. hydrogenation bomb at 150° under 1500 p.s.i. of hydrogen. The catalyst was removed by filtration and distillation gave 69.5 g. (65.6%) of a colorless oil, b.p. 79–80° (0.7 mm.), $n^{22}\mathrm{D}$ 1.4596, $\nu_{\max}$ 2.90 and 5.88 μ. Vapor phase chromatography on a Carbowax 20M column indicated the presence of a mixture of stereoisomers.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.59; H, 9.66.

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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}_{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}_{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}_{D} 1.4856; $\lambda^{\mathrm{alc}}_{\max}$ 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}_{D} 1.4846[4]; b.p. 101–103° (10 mm.), n^{20}_{D} 1.4845[5]; and b.p. 95–96° (11 mm.), n^{20}_{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}_{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}_{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}_{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}_{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}_{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}_{D} 1.4919[5]; b.p. 103.5–104.5° (24 mm.), n^{20}_{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}_{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}_{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}_{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}_{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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The Preparation of $\Delta^{9,10}$-Octalin-2,7-dione

PHILLIP RADLICK

Department of Chemistry, University of California,
Riverside, California 92502

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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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