15.85 g. (41%) of 1-methylcyclohexene, b.p. 109–109.5°, n^{25}D 1.4509 (lit.[32] 109.5°, n^{20}D 1.4505). Extraction of the olefin was not quantitative as shown in a blank experiment; authentic 1-methylcyclohexene (Aldrich, distilled), subjected to the same isolation procedure, was recovered in 70% yield.

Reduction of 2α-Bromocholestanone.—To a 100-ml. three-necked flask containing a magnetic stirrer and attached through a condenser to a gas buret were added 13 ml. (0.4 mole) of hydrazine hydrate, 2 g. (20 mmoles) of potassium acetate, and 10 ml. of cyclohexene. The flask was heated until the cyclohexene boiled, and a solution of 2.004 g. (4.3 mmoles) of 2α-bromocholestanone in 30 ml. of cyclohexene was added dropwise over 10 min. while maintaining stirring and boiling. Heating was continued for 30 min. The light yellow mixture was cooled, extracted with ether–water, dried, evaporated, dissolved in hexane, and percolated through a column of acid-washed alumina (Merck). Evaporation of the filtrate yielded 995 mg. (64%) of 2-cholestene, m.p. 72–74°, $[\alpha]_D$ +64°. Recrystallization from ether–ethanol (2:1) gave white needles of 2-cholestene in 95% yield, m.p. 73–75°, $[\alpha]_D$ +65°.

Poorer results were obtained if the reagents were all mixed before heating. Thus a mixture of 2.009 g. of 2α-bromocholestanone, 13 ml. of hydrazine hydrate, 2 g. of potassium acetate, and 13 ml. of cyclohexene heated to reflux yielded a darker reaction mixture and only 269 mg. (19%) of 2-cholestene, m.p. 72–74°.

2α,3β-Dibromocholestane.—To a solution of 109 mg. (0.29 mmole) of 2-cholestene, m.p. 73–75°, in 2 ml. of ether was added dropwise a solution of bromine in acetic acid until a slight excess of bromine was present. Evaporation of solvent and crystallization of the residue from ether–ethanol gave 76 mg. (49%) of white plates of 2α,3β-dibromocholestane, m.p. 123–124°, lit.[28] m.p. 125°.

Hydrogenation of 2-Cholestene.—Microhydrogenation of 40.6 mg. (0.11 mmole) of 2-cholestene, m.p. 72–74°, in acetic acid using 10% palladium on carbon as catalyst, led to the slow (*ca.* 6 hr.) uptake of 1.00 equivalent of hydrogen. Work-up of the solution gave a light yellow residue which was dissolved in hexane and percolated through a short alumina column. Evaporation of the filtrate yielded 34 mg. (85%) of crude cholestane, m.p. 75–80°. The melting point was raised to 79–80°, lit.[28] m.p. 80°, by crystallization from ether–ethanol.

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[32] G. Egloff, "Physical Constants of Hydrocarbons," Vol. 2, Reinhold Publishing Corp., New York, N. Y., 1940, p. 326.

Tropone. Selenium Dioxide Oxidation of 1,3,5-Cycloheptatriene

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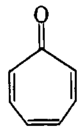
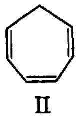
There are several methods known for the preparation of tropone (2,4,6-cycloheptatrien-1-one, I).[1-5] They range in scope from the degradation of tropinone[4] to produce I, to the formation of bis-2,4,6-cycloheptatrien-1-yl ether (III) from the hydrolysis of tropilium salts and subsequent disproportionation of the ether to give I and 1,3,5-cycloheptatriene (II).[2,3]



I



II

We have observed a direct oxidation of II by selenium dioxide in buffered aqueous dioxane to give I in about 25% yield. This reaction, though not high in yield, affords a simple one-step preparation of I from commercially available starting materials. The reaction can readily be adapted to large scale, and the inorganic product, selenium, can be recovered and reoxidized to selenium dioxide if desirable.[6]

Experimental

Preparation of Tropone.—To a solution of potassium dihydrogenphosphate (13.5 g., 0.1 mole) in water (33 ml.) was added 1,4-dioxane (330 ml.), 1,3,5-cycloheptatriene (43.0 g., 0.46 mole, Shell Chemical Corp., contained 6% toluene), and selenium dioxide (53.0 g., 0.48 mole, Matheson, Coleman and Bell). The mixture was warmed on the steam bath (90°) for 15 hr., allowed to cool to room temperature, and then filtered. The filtrate was poured into water (750 ml.) and extracted three times with 250-ml. portions of methylene chloride. The organic extract was washed with 10% sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to a dark brown liquid. Distillation of this liquid gave 12.8 g. (25%) of pale yellow tropone, b.p. 91–92° at 4 mm., n^{23}D 1.6152. The infrared spectrum of this material was identical with that reported by Doering.[5]

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The Reaction of Chlorocarbene with Styrene

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A number of carbenes or "carbene-like" species have been added to styrene to give substituted phenylcyclopropanes.[1] Closs and co-workers[2] have generated chlorocarbene from methylene chloride and methyl- or *n*-butyllithium and added it to various olefins to give substituted chlorocyclopropanes. The work which is now reported was undertaken to study the addition of chlorocarbene to styrene.

When ethereal *n*-butyllithium, prepared from *n*-butyl bromide and lithium, was allowed to react with methylene chloride in the presence of excess styrene, two stereoisomeric 1-chloro-2-phenylcyclopropanes were isolated in low yields in addition to several gaseous products. The yields of **1** (4.1%) and **2** (4.9%) are based on distilled material, assuming equal thermal conductivities on gas chromatographic (g.c.) analysis. The structural

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