derivative of cyclopentanone, the latter underwent self-condensation to form III and IV. The 2-cyclopentylidenecyclopentanone (IV) then reacted with 1-acetylcyclohexene to give II. As a confirmation of structure, IV was prepared[6] and treated with 1-acetylcyclohexene in the presence of sodamide by analog with earlier work[4] to form II in 40% yield. A 2,4-dinitrophenylhydrazone of II was prepared. Also, the absorption maximum of II in the ultraviolet was found to be at 308 mμ; a value of 316 was calculated by the rule of Woodward for conjugated dienones.[7]

Compound II is a substituted α-decalone prepared under alkaline conditions where only the *trans*- form has been considered to be stable.[8] Thus, II may have *trans*- ring fusion between the rings corresponding to rings B and C in the steroid series where the same stereochemical arrangement was established. However, since no proof is available, it is preferred to leave the question open.

EXPERIMENTAL

Attempted synthesis of 5-keto-$\Delta^{3a(4)}$-decahydro-1-benz[e]indene (I). Cyclopentanone and 1-acetylcyclohexene[9] in 0.08 molar amounts were used under conditions suggested by the work of Birch and Robinson.[4b] Distillation of the ether soluble material gave 5 g. of a yellow oil which distilled at 75–150° (0.3 mm.). Redistillation gave 2 g. of oil of b.p. 125° (0.3 mm.) which solidified, m.p. 82–84°. After several recrystallizations from methyl alcohol the yellow *2,5-dicyclopentylidenecyclopentanone* (III) melted at 89–90°. Admixture of this compound with III of the same melting point, obtained from cyclopentanone in the presence of sodium ethoxide[6], did not depress the melting point [lit., b.p. 190° (12 mm.)[6a]; m.p. 76–77°[6a]; b.p. 198–200° (12 mm.)[6b]; m.p. 81.5–82°[6b]]. The substance would not readily form a ketonic derivative, and, after a few days, it darkened badly.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.02; H, 9.35.

Continued distillation at 150–170° (0.3 mm.) gave 1 g. of highly viscous, oily *3-cyclopentylidene-5-keto-$\Delta^{3a(4)}$-decahydro-1-benz[e]indene* (II) which crystallized upon treatment with acetone, m.p. 161–164°. After several recrystallizations from acetone, the white needles melted at 167–169°.

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.48; H, 9.41.

3-Cyclopentylidene-5-keto-$\Delta^{3a(4)}$-decahydro-1-benz[e]indene (II). To a suspension of 3 g. (0.077 mole) of sodamide in 180 ml. of dry ether in a nitrogen atmosphere, 11.6 g. (0.073 mole) of 2-cyclopentylidenecyclopentanone (IV)[6] was added with stirring and cooling during a period of 15 min. The mixture stood then for 6 hr. at room temperature and was finally refluxed for 1 hr. With stirring and cooling 9.6 g. (0.077 mole) of 1-acetylcyclohexene was added. After standing overnight, the mixture was treated with 60 ml. of dilute sulfuric acid and then extracted with ether. The extract was handled in the usual manner to give 7.9 g. (40% yield) of crude II, b.p. 155–184° (0.3 mm.). After several recrystallizations from acetone, it melted at 167–169° and the melting point was not depressed by samples obtained earlier (*vide supra*). (λ_{max}^{EtOH} 308 mμ, ε 1.42 × 10^5; λ_{min}^{EtOH} 250 mμ, ε 4.03 × 10^4.)

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.52; H, 9.54.

The *2,4-dinitrophenylhydrazone of II* was prepared and recrystallized from chloroform as a red crystalline solid, m.p. 243–245° dec.

Anal. Calcd. for $C_{24}H_{28}N_4O_4$: C, 66.03; H, 6.47. Found: C, 65.87; H, 6.52.

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Steroidal Hormone Relatives. VII. Allylic Bromination of *trans*-9-Keto-Δ^{10},-decahydrophenanthrene[1]

J. H. BURCKHALTER AND P. KURATH[2]

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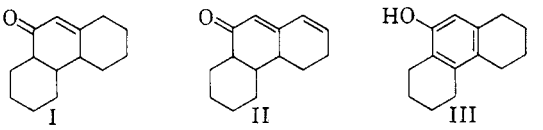
A further search for a cyclic α,β-unsaturated ketone as a model compound which would offer a possibility for bromination in the allylic position corresponding to C-17 of the steroids[3] resulted in the selection of *trans*-9-keto-Δ^{10}-dodecahydrophenanthrene (I).[4]



Reaction of I with *N*-bromosuccinimide in the absence of ultraviolet irradiation, according to the experimental procedure of Meystre and Wettstein,[5] followed by treatment of the crude bromination product with cuprous cyanide,[6] yielded a mixture from which no pure product was isolated. However, since hydrogen bromide was formed during the bromination step, it was decided that bromination had occurred and was followed by the introduction into I of a second carbon-to-carbon double bond.

A repetition of the bromination experiment, followed by a dehydrobromination procedure em-

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ploying pyridine,[7] gave a mixture which was separated through distillation and recrystallization into two isomeric compounds considered to be 9-keto-$\Delta^{1,10}$-decahydrophenanthrene (II) and *sym*-octahydro-9-phenanthrol (III).

Mixed melting point determinations showed that I, II and III were distinct. Although neither product gave a positive ferric chloride test, the phenolic compound (III) was slightly soluble in 10% sodium hydroxide solution and had the same melting point as the previously described III prepared by different procedures.[8] Also, the infrared absorption spectrum of III showed a strong peak at 3.13 μ, indicative of a hydroxyl, and weaker peaks at 6.20, 6.32, and 6.67, indicative of a monohydroxyphenyl grouping. II showed strong carbonyl absorption (6.13 μ) in the infrared and absorption of less intensity at 6.33 suggestive of conjugated C=C groupings. Absorption maximum of II in the ultraviolet was at 286 mμ, which compares favorably with the value of 280 calculated by the rule of Woodward and found for the analogous $\Delta^{3,5}$-cholestadiene-7-one.[9] It is possible that II may have a double bond between positions 4 and 4a instead of 1 and 2. However, Woodward's rule gives 298, a less favorable value than 280.

The isolation of compounds of structures II and III suggests that the allylic bromination of I occurred at positions 1 and 4a. II probably arises from loss of hydrogen bromide at positions 1 and 2 and III from loss at 4a and 5a.

EXPERIMENTAL

Reaction of trans-9-keto-Δ^{10}-dodecahydrophenanthrene (I) *with N-bromosuccinimide.* A mixture of 6 g. (0.029 mole) of I, 15.8 g. (0.066 mole) of *N*-bromosuccinimide and 100 ml. of carbon tetrachloride was heated at reflux temperature for 90 min. The solvent was removed by distillation and replaced with 100 ml. of pyridine, whereupon heating at boiling temperature was continued for 2 hr. The pyridine was removed under reduced pressure and the residue dissolved in ether. After the ether extract was washed with 2*N* hydrochloric acid and then water, it was dried over magnesium sulfate and the ether removed. Upon distillation of the residue, 3 g. of crude 9-keto-$\Delta^{1,10}$-decahydrophenanthrene (II) was obtained at 145–150° (0.2 mm.). The solidified residue was recrystallized first from methyl alcohol and then from acetone, m.p. 119–121° (λ_{max}^{EtOH} 286 mμ, ϵ 1 × 10^4; λ_{min}^{EtOH} 270 mμ).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.11; H, 8.97. Found: C, 83.03; H, 9.55.

Continued distillation at 150–155° (0.2 mm.) gave 1 g. of oil which solidified. After removal of the mother liquors from the isolation of II, the residue was combined with the solid distillate and distilled to give 2.1 g. of solid product, b.p. 155° (0.2 mm.). Upon recrystallization from methyl alcohol, a small amount of II separated. On standing, the filtrate yielded a higher melting compound. Recrystallization from dilute methyl alcohol gave a small amount of *sym*-octahydro-9-phenanthrol (III), m.p. 133–134° (lit.[8] 133°).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.11; H, 8.97. Found: C, 83.66; H, 9.12.

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The Synthesis of 7-Halogeno-1-hydroxy-2-naphthoic Acids

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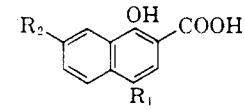
This report deals with the preparation of 1-naphthol derivatives with substitutions in the difficultly accessible 7-position.[1,2] The procedure employed for the preparation of the desired compounds involved the cyclization of a γ-substituted phenylbutyric acid to a 7-substituted-1-tetralone, followed by bromination and dehydrobromination to the naphthol. This product was carboxylated by a modified Kolbe procedure with subsequent chlorination in the 4-position.

Although somewhat lengthy, the procedure adopted has given unequivocally the desired modified naphthoic acids. Of special interest is the action of dimethyl formamide and lithium chloride as a dehydrohalogenating agent. This reagent was employed by Holyz[3] for introducing α, β-unsaturation in 3-keto steroids, and has recently been used by Gabel and Binkley[4] in the dehydrobromination of bromodihydropyrimidines to pyrimidines. The present application to bromotetralones indicates the general usefulness of this method. According to Holyz the lithium chloride is an obligatory factor for the activation of the bromine atom.

Four new 1-hydroxy-2-naphthoic acids have been synthesized and characterized. The effect of these



R_1 = hydrogen or chlorine
R_2 = bromine or chlorine

compounds and their derivatives on oxidative phosphorylation in rat brain mitochondria was studied and it was observed that both a free carboxyl group and a free hydroxyl group were necessary for inhibition of this process.

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