(0.7 mole) of finely powdered ammonium carbonate monohydrate and 400 ml. of acetone. From a dropping funnel, 126 g. (0.5 mole) of diphenyldichlorosilane dissolved in 150 ml. of acetone was added portionwise into the flask, which was shaken gently during the addition. By the addition, ammonium chloride precipitated as fine white crystals and carbon dioxide was evolved readily; the gas evolved from the reaction mixture immediately precipitated barium carbonate when it was led into barium hydroxide aqueous solution. After the addition was complete, the contents were refluxed gently for about 1 hr. The product was filtered by suction after cooling and the colorless filtrate was then evaporated to dryness on a water bath; a white needle crystalline mass melting at 122–126° was obtained. Further purification was effected by recrystallization from purified methylacetate; 100 g. (93%) of white needles were obtained.

Anal. Calcd. for $C_{12}H_{12}SiO_2$: C, 66.62; H, 5.59; Si, 12.97; mol. wt., 216; OH/molecule, 2.00. Found: C, 66.3; H, 5.20; Si, 12.8; mol. wt., 190–198 (glacial acetic acid); OH/molecule, 1.97 (Karl Fischer titration[8]).

Density of a single crystal when measured in calcium chloride aqueous solution of matched density was 1.16 (at 25°).

The infrared absorption data were in complete agreement with those given by Tatlock and Rochow.[9]

Regarding the melting point of this diol, the well known abnormality was confirmed: For example, needles obtained from acetone ether melted at 155°, needles from methylacetate melted at 147–148°; moreover, some needles which melted at 131–133°, 142–144°, 158–160° were also found during many measurements. Melting was always accompanied by formation of liquid decomposition products and the measurement of melting point was always carried out using clean Pyrex capillary tube and at the rate of heating 5° per min., the bath being preheated at about 110°.

Further investigations on the possible existence of poly- or mesomorphism of this diol are being undertaken by using x-ray technique.

Cyclodiphenylsiloxanes. (A) *Trimer.* The crude crystalline mass obtained in the procedure described above was dissolved in 1000 ml. of ether, and 30 ml. of concentrated hydrochloric acid was added. The mixture was gently refluxed or about 2 hr. and then evaporated to dryness on a water bath. Recrystallization from ethanol benzene gave 75 g. (77%) of hexaphenylcyclotrisiloxane melting at 189°.

(B) *Tetramer.* The filtrate obtained in the above procedure was concentrated in the presence of a small grain of sodium hydroxide. White crystals precipitated upon cooling; recrystallization from ethylacetate gave 81 g. (82%) of octaphenylcyclotetrasiloxane melting at 201°.

These cyclodiphenylsiloxanes were well identified by their x-ray powder pattern data.[10]

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Steroidal Hormone Relatives. VI. The Condensation of Cyclopentanone with 1-Acetylcyclohexene[1]

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

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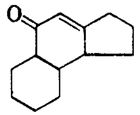
This report describes part of a continuing program in the synthesis of model compounds which contain a carbonyl group in a position corresponding to the 11-keto of cortisone.[3] In the present approach, 1-acetylcyclohexene was condensed with cyclopentanone under alkaline conditions in an effort to obtain a Michael reaction product which would then undergo an aldol type reaction to give 5-keto-$\Delta^{3a(4)}$-decahydro-1-benz[*e*]indene (I).[4] Compound I would offer a possibility for bromination in the allylic position[5] corresponding to C-17 of the steroids and thus open a route to the dihydroxyacetone side chain of cortisone.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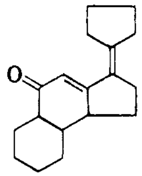
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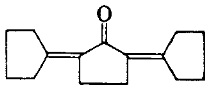
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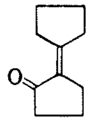
IV

Various attempts to obtain I by the condensation of 1-acetylcyclohexene and cyclopentanone in the presence of sodamide in ether,[4a] lithium amide in ether,[4b] sodium in an excess of cyclopentanone,[4c] and potassium isopropoxide in pyridine,[4d] yielded instead of I a mixture of 3-cyclopentylidene-5-keto-$\Delta^{3a(4)}$-decahydro-1-benz[*e*]indene (II) and 2,5-dicyclopentylidenecyclopentanone (III).

It has been pointed out by Wallach that cyclopentanone condenses with itself in the presence of sodium ethoxide to form III and 2-cyclopentylidenecyclopentanone (IV).[6] It appears that under the conditions employed to prepare the alkali metal

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(1) Aided by the General Research Fund, University of Kansas.

(2) Abbott Laboratories, North Chicago, Ill.

(3) J. H. Burckhalter and P. Kurath, *J. Am. Chem. Soc.*, **81**, 395 (1959).

(4) Earlier approaches in this direction may be seen in the studies of Robinson and others: (a) W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1285 (1935); (b) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 503 (1944); (c) C. A. Friedmann and R. Robinson, *Chem. and Ind.* (*London*), 777 (1951); and (d) W. Huber, *Ber.*, **71**, 725 (1938).

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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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(9) J. H. Saunders, *Org. Syntheses*, Coll. Vol. III, 22 (1955).

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

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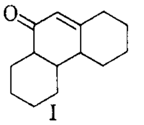
A further search for a cyclic α,β-unsaturated ketone as a model compound which would offer a possibility for bromination in the allylic position corresponding to C-17 of the steroids[3] resulted in the selection of *trans*-9-keto-Δ^{10}-dodecahydrophenanthrene (I).[4]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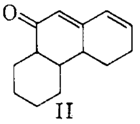
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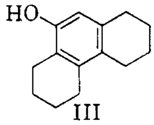
III

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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(1) Aided by the General Research Fund, University of Kansas.

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