Exactly 5 g. of urea, C.P., was caused to react with excess acetone as in the first experiment. A specimen of this urea was investigated. Film #23 did not show much evidence for hexagonal urea. Film #42 did show a weak line at about 21° 12/(20). This corresponds to the most intense line of the hexagonal urea adduct, Film #35. The intense line of tetragonal urea was very dark on the film because of the long exposure. A densitometer was used to compare the line of the hexagonal with the intense line of the tetragonal urea. Only an estimate could be made on account of the high darkening of the tetragonal line. This estimate put the amount of hexagonal urea at probably less than 5%. Diffraction patterns are shown in Fig. 3.

DISCUSSION

The existence of the small portion of hexagonal urea, after the acetone urea adduct is decomposed by heating the adduct, could perhaps justify a conjecture that the hexagonal channels of urea do not all collapse instantly upon the escape of the acetone molecules. Some of them may retain their hexagonal configuration or assume some metastable structure before reverting to the natural tetragonal form. Such a crystalline configuration would favor adduct formation with adduct forming substances without the use of a urea solvent. A phenomenon similar to adsorption[6] may take place when acetone activated urea is contacted with a substance such as oleic acid. The catalytic effect of acetone, and perhaps of other ketones, may be explainable not only on the basis that acetone is a mutual solvent for both urea and adduct forming substances but also that it forms its urea adduct which decomposes to provide *in situ* acetone activated urea.

Acknowledgment. We thank Mr. H. D. Orcutt of the Physics Research Dept. of Aerojet General Corp., who did the x-ray work, for his interest and helpful advice. We also express gratitude to Pacific Vegetable Oil Corp., for offering to us the opportunity to become interested in this study.

AEROJET-GENERAL CORP.
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New Simple Preparation of Diphenylsilanediol and Its Condensation Products; Cyclodiphenylsiloxanes

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In the previous works[1–7] related to the preparation of diphenylsilanediol (hereafter called diol) from diphenyldichlorosilane, the hydrolysis of the chlorosilane under carefully controlled mild conditions to minimize the formation of high polymers has generally been aimed at for successful preparation.

The author now finds that diol in pure form can be obtained readily from the reaction of diphenyldichlorosilane with ammonium carbonate monohydrate, the yield being 90–94%.

The new method can be represented summarily by the following equation:

$$(C_6H_5)_2SiCl_2 + (NH_4)_2CO_3\text{-}H_2O \longrightarrow (C_6H_5)_2Si(OH)_2 + 2NH_4Cl + CO_2$$

When 1 mole of diphenyldichlorosilane was added to 1.2–1.5 mole of ammonium carbonate monohydrate covered with an inert anhydrous organic solvent preheated at 50–60°, the ammonium salt decomposed readily, evolving carbon dioxide, and ammonium chloride precipitated as fine crystals. After cooling to room temperature, the reaction product was filtered, whereupon pure diol was obtained from the filtrate upon evaporation. The most effective result was obtained by use of acetone as the reaction medium: The hydrophilic character of this would make the first stage of the reaction, hydrolysis of diphenyldichlorosilane with water produced by the decomposition of ammonium carbonate, fairly homogeneous.

The proposed method has the advantage that throughout the preparation procedure no byproducts other than ammonium chloride and carbon dioxide were produced. Both of these have no disadvantageous effect on the hydrolysed product and can be separated easily from the liquid part, allowing ready isolation of diol.

As has been described by Burkhard,[4] diol was converted readily into cyclodiphenylsiloxanes on being refluxed in an appropriate solvent in the presence of acid or caustic alkali as catalyser; hydrochloric acid and sodium hydroxide gave hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane, respectively.

EXPERIMENTAL

Reagents. Reagent grade ammonium carbonate monohydrate was used after prolonged drying in a vacuum desiccator. Highest purity diphenyldichlorosilane was received from the Shin-etsu Chemical Industrial Co. Acetone was purified according to the ordinary method.

Preparation and some properties of diol. In a 2-l. flask surrounded by a water bath heated at 50° was placed 80 g.

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(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]

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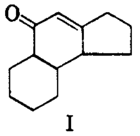
This report describes part of a continuing program in the synthesis of model compounds which contain a carbonyl group in a position corresponding to the 11-keto of cortisone.[3] In the present approach, 1-acetylcyclohexene was condensed with cyclopentanone under alkaline conditions in an effort to obtain 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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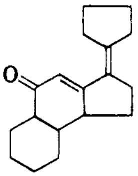
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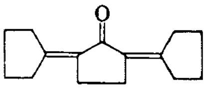
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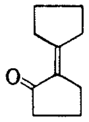
IV

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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