0.25 ml. of 0.2 molar chloroplatinic acid in ethanol was refluxed for 4 hr. A slow stream of an inflammable gas presumed to be silane was observed. Absolute ethanol (50 ml.) was then added, and the mixture was distilled to give 26.7 g. of tetraethoxysilane, b.p. 80–90° at 29 mm., n_D^{25} 1.3850, and 94 g. of II (61% yield), b.p. 119–122° at 29 mm., n_D^{25} 1.4220, D_4^{25} 0.9477, R_D calcd. 0.2670, R_D found 0.2676. Jex and Bailey[2] reported b.p. 123° at 30 mm., n_D^{25} 1.4195, D^{25} 0.942.

Anal. Calcd. for $C_9H_{23}NO_3Si$: Si, 12.61; neut. equiv. 221. Found: Si, 12.39; neut. equiv. 221.

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (III). *sym*-Tetramethyldisiloxane (134 g.) was added slowly to refluxing allylaminotrimethylsilane (294 g.) which contained 0.2 ml. of 0.22 molar chloroplatidic acid in ethanol. After the reaction was initiated, the temperature of the mixture was maintained at 110° to 125° by regulating the rate of addition of the siloxane. After the reaction was complete, 100 ml. of absolute ethanol was added and the lower boiling components were distilled from the mixture. The residue was distilled at reduced pressure to give 191 g. (78% yield) of III, b.p. 96–104° at 2.5 mm., b.p. 134–142° at 11.5 mm., n_D^{25} 1.4475–1.4485, D_4^{25} 0.8956–0.8971. R_D calcd. 0.2995, R_D found 0.2989–0.2987.

Anal. Calcd. for $C_{10}H_{28}ON_2Si_2$: Si, 22.60; neut. equiv., 124. Found: Si, 22.38; neut. equiv., 124.5.

A solution of 4.5 g. of III in 200 ml. of anhydrous ether was saturated with dry hydrogen chloride to form the dihydrochloride. Recrystallized twice from ethyl acetate, 1,3-bis(3-aminopropyl)tetramethyldisiloxane dihydrochloride had a m.p. of 250–253°.

Anal. Calcd. for $C_{10}H_{30}ON_2Cl_2Si_2$: Si, 17.45. Found: Si, 17.69.

3-Chloropropyldimethylethoxysilane (IV). To a stirred solution of 252 g. of 3-chloropropyldimethylchlorosilane in 750 ml. of hexane was added 138 g. of absolute ethanol through a tube extending beneath the surface of the liquid. The mixture was refluxed for 2.5 hr., saturated with anhydrous ammonia, and filtered. The precipitate was washed with hexane, and the solvent was removed from the combined filtrates by distillation. The residue was distilled at reduced pressure to give 188.1 g. (69%) of IV. Boiling point 87° at 30 mm., n_D^{25} 1.4270, D_4^{25} 0.9319, R_D calcd. 0.2759, found 0.2755.

Anal. Calcd. for $C_7H_{17}OClSi$: Si, 15.50. Found: Si, 15.54.

3-(Ethoxydimethylsilyl)propylamine (V). A mixture of 90 g. of 3-chloropropyldimethylethoxysilane (IV) and 204 g. of anhydrous ammonia was heated at 95° for 2 hr. in a 1-l. stainless steel bomb. After the bomb was cooled the organic layer was separated from the ammonia-ammonium chloride layer; and a 52.5 g. portion of the product was distilled at reduced pressure to give 25.7 g. of 3-ethoxydimethylsilylpropylamine. Boiling point 79–78° at 24 mm., n_D^{25} 1.4276, D_4^{25} 0.8570. R_D calcd. 0.3004, found R_D 0.2999.

Anal. Calcd. for $C_7H_{19}ONSi$: Si, 17.39; neut. equiv., 161. Found: Si, 17.17; neut. equiv., 160.2.

A mixture of 16 g. of 3-ethoxydimethylsilylpropylamine, 20 ml. of water and 5 g. of potassium hydroxide was extracted with two 20-ml. portions of ether. The ether solution was dried over potassium hydroxide. A 10-ml. portion saturated with dry hydrogen chloride gave 4.15 g. of 1,3-bis(3-aminopropyl)tetramethyldisiloxane dihydrochloride, m.p. 249.5–251.5° from ethanol–ethyl acetate.

Anal. Calcd. for $C_{10}H_{30}ON_2Cl_2Si_2$: Si, 17.45. Found: Si, 17.39.

The remainder of the ether solution was evaporated to yield 10 g. of 1,3-bis(3-aminopropyl)tetramethyldisiloxane, n_D^{25} 1.4480, D_4^{25} 0.8960, R_D calcd. 0.2995, R_D found 0.2988.

Anal. Calcd. for $C_{10}H_{28}ON_2Si_2$: neut. equiv. 124. Found: neut. equiv. 124.6.

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2,5-Dibenzylidene-3-cyclopentenone

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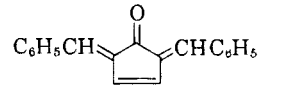
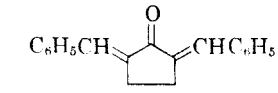
In an investigation of the photochemical properties of 2,5-dibenzylidene-3-cyclopentenone (I), we have encountered unambiguous evidence that I as previously prepared[1] is contaminated with 2,5-dibenzylidenecyclopentanone (II). This impurity was not removed by repeated recrystallization from a variety of solvents. Furthermore, the mixture of I and II gave satisfactory carbon, hydrogen analyses for I. General interest in the unique structure of 2,5-dibenzylidene-3-cyclopentenone has prompted us to relate this evidence together with a



I



II

novel procedure for the elimination of the contaminant.

The unexpected presence of II was first detected in an attempt to prepare the uranyl chloride complex of I. Treatment of a hot, saturated solution of supposedly pure I[2] with uranyl chloride gave in low yield an orange-red, crystalline complex. This complex had an infrared spectrum identical to that of an authentic sample of the uranyl chloride-2,5-dibenzylidenecyclopentanone complex.[3] The complex on dissolution in ethanol precipitated a yellow ketone which was shown by mixed melting point and infrared and ultraviolet spectral identity to be 2,5-dibenzylidenecyclopentanone thus confirming the identity of the contaminant. Cooling of the filtrate, after removal of the highly insoluble complex, gave I, m.p. 156–157° (reported previously,[1] m.p. 150°). A second treatment of I with uranyl chloride gave no complex, and the 2,5-dibenzylidene-3-cyclopentenone recovered had melting point, infrared and ultraviolet absorption identical to those of I after a single treatment with uranyl chloride. 2,5-Dibenzylidene-3-cyclopentenone thus purified showed λ_{max}^{EtOH} 316 mμ (38,900) and 232–234 mμ (11,700).

The failure of I to form a uranyl chloride complex strongly supports the geometric configuration suggested for I by Wanzlick.[1] The structure of the uranyl chloride-2,5-dibenzylidene cycloalkanone complexes will be discussed in a forthcoming report of their photochemical transformations.

EXPERIMENTAL

2,5-Dibenzylidene-3-cyclopentenone (I) (*after Wanzlick*[1]). A solution of 2,5-dibenzylidenecyclopentanone (26 g., 0.1 mole)

(1) H. Wanzlick, *Chem. Ber.*, **86**, 41 (1953).
(2) This material (m.p. 150°) had been recrystallized seven times from trichloroethylene.
(3) P. Pretorius and F. Korn, *Ber.*, **43**, 2744 (1910).

and *N*-bromosuccinimide (19.6 g., 0.11 mole) in 450 ml. of carbon tetrachloride was stirred and irradiated with a General Electric RS sunlamp for 2 hr. During this time, hydrogen bromide was evolved, and by the end of this period the solution had developed a dull red color. The succinimide was removed by filtration. The filtrate was evaporated to a pasty residue. Recrystallization of the residue from trichloroethylene gave greenish-yellow crystals, m.p. 150°, yield (13 g., 50%). Additional recrystallization of this material from trichloroethylene, benzene, xylene, or acetic acid–acetone (1:1) did not alter the melting point.

Purification of 2,5-dibenzylidene-3-cyclopentenone (I). The product I (14.7 g., 0.093 mole, m.p. 150°) described above was dissolved in the least possible volume of hot acetic acid–acetone (1:1). Uranyl acetate dihydrate (10 g.) dissolved in 3.8 ml. of hydrochloric acid was added to the hot solution. An orange-red precipitate began to form immediately. The solution was protected from light with aluminum foil and kept hot for 2 hr. The precipitated complex was filtered from the hot solution. This gave orange-red crystals (4.3 g., 5%) which did not melt below 300° and which showed infrared maxima identical to those of an authentic sample of the uranyl chloride-2,5-dibenzylidenecyclopentanone complex[3] (both spectra were taken in potassium bromide). Cooling of the filtrate gave greenish-yellow plates, m.p. 156–157°. This material gave, after two recrystallizations from trichloroethylene, 9 g. of I, m.p. 156–157°, λ_{max}^{EtOH} 316 mμ (38,900) and 232–234 mμ (11,700).

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.45. Found: C, 88.12; H, 5.57.

2,5-Dibenzylidene-3-cyclopentenone thus purified did not give a precipitate on further treatment with uranyl chloride, and the material recovered from this second treatment had the same melting point, infrared spectrum, and ultraviolet spectrum as I purified by a single treatment with uranyl chloride.

Recovery of 2,5-dibenzylidenecyclopentanone from the uranyl chloride complex. The complex obtained above was washed with benzene to remove any organic material which had coprecipitated with it, and then warmed in ethanol with stirring until all of the orange-red complex had disappeared. During this process, a yellow precipitate formed which was collected by filtration and recrystallized from benzene giving bright yellow needles, m.p. 182–186° (authentic 2,5-dibenzylidenecyclopentanone m.p. 188–190°), mixed melting point with 2,5-dibenzylidenecyclopentanone 185–190°. This material had infrared and ultraviolet absorption spectra identical to those of authentic 2,5-dibenzylidenecyclopentanone.

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Synthesis of 7-Methyl Steroid Hormones. II. 7β-Methylcortisone Acetate and 7β-Methylhydrocortisone Acetate

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While a considerable number of alkylated steroid hormones have been described in recent years[1] no 7-alkylated cortisone derivatives have been prepared, and we therefore felt that the synthesis of these compounds would be of interest.

The effect on cortical activity associated with the substitution of methyl groups, or halogen (particularly fluorine) atoms, in place of hydrogen in the A, B, and C rings has been reviewed recently,[2] and may be summarized as follows.

If the methyl group or halogen atom is in an α-axial or α-equatorial configuration (2α-,[3] 6α-,[4] 9α-,[5] 12α-[6]) then retention or enhancement of physiological activity is observed.[7]

The paucity of β-axial and β-equatorial substituted corticoids prevents any generalization. The 6β-methyl- and halo-corticoids have been described, and it is established that these are less active than the parent compounds.[2] The only other case of a β-axial methyl substituted hormone is 8β,14α-dimethyl-18-nortestosterone[8] which is inactive as an androgen.

The 7β-methyl compounds described in this work provide the first example of *β-equatorial* substitution by methyl in corticoids[9] and it is therefore interesting to note that activity is lowered by such substitution.

An obvious starting point for the synthesis was the 3,20-bisethylene ketal of 7-ketocortisone acetate (II). Attempts to prepare (II) by *tert*-butyl chromate oxidation of the 3,20-bisethylene ketal (I)[10] led, in poor yield, to a substance showing an

(1) See Part I (C. H. Robinson, Olga Gnoj, W. Charney, M. L. Gilmore, and E. P. Oliveto, *J. Am. Chem. Soc.*, in press) for pertinent references.

(2) J. A. Hogg, 6th National Medicinal Chemistry Symposium of the American Chemical Society, Madison, Wis., June 23–25, 1958.

(3) J. A. Hogg, F. H. Lincoln, R. W. Jackson, and W. P. Schneider, *J. Am. Chem. Soc.*, **77**, 6401 (1955).

(4) G. B. Spero, J. L. Thompson, B. J. Magerlein, A. R. Hanze, H. C. Murray, O. K. Sebek, and J. A. Hogg, *J. Am. Chem. Soc.*, **78**, 6213 (1956). See also G. B. Spero, J. L. Thompson, F. H. Lincoln, W. P. Schneider, and J. A. Hogg, *J. Am. Chem. Soc.*, **79**, 1515 (1957).

(5) J. Fried and E. Sabo, *J. Am. Chem. Soc.*, **79**, 1130 (1957).

(6) D. Taub, R. D. Hofsommer, and N. L. Wendler, *J. Am. Chem. Soc.*, **79**, 452 (1957).

(7) In apparent contradiction to this generalization, 11α-methylhydrocortisone acetate [G. S. Fonken and J. A. Hogg, *Tetrahedron*, **2**, 367 (1958)] is less active than the parent hydrocortisone acetate. However, the methyl group here has been introduced at the carbon bearing the 11β-hydroxyl group, and so the substitution differs from the others described which are α-, or vinylogously α-, to oxygen atoms at C-3 or C-11.

(8) P. Crabbé, G. Ourisson, and T. Takahashi, *Tetrahedron*, in press. J. F. Biellman, P. Crabbé, and G. Ourisson, *Tetrahedron*, in press.

(9) A patent has now appeared [J. C. Babcock and J. A. Campbell, U. S. Patent **2,838,534** (1958)] which outlines the preparation of 7-methyl cortical hormones. However, 7-methylcortisone and hydrocortisone are partially or not at all characterized, and no stereochemistry is assigned.

(10) See, for example, P. N. Rao and P. Kurath, *J. Am. Chem. Soc.*, **78**, 5660 (1956) and C. W. Marshall, R. E. Ray, I. Laos, and B. Riegel, *J. Am. Chem. Soc.*, **79**, 6308 (1957).