stances toward electrophilic substitution as judged by ease of acylation[7] and by competitive acetylations.[8] The reactivity order in this case is ferrocene > ruthenocene > osmocene.

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[7] M. D. Rausch, E. O. Fischer and H. Grubert, *Chem. and Ind.*, 756 (1958).

[8] J. H. Richards and D. C. Garwood, unpublished results.

[9] National Science Foundation Predoctoral Fellow.

RECEIVED MAY 6, 1959

STEROIDS. CXXVII.[1] 6-HALO PROGESTATIONAL AGENTS

Sir:

17α-Acetoxyprogesterone 3-ethyl enol ether (I) (m.p. 160–163°, $[\alpha]_D$ −146° (all rot. in $CHCl_3$), λ_{max}^{EtOH} 241 mμ, log ε 4.32)[2] on reaction with N-chlorosuccinimide gave 6β-chloro-17α-acetoxyprogesterone (A = 0.5)[3] (m.p. 221–222°, $[\alpha]_D$ −10°, λ_{max} 239 mμ, log ε 4.19) inverted by hydrogen chloride–acetic acid to 6α-chloro-17α-acetoxyprogesterone (II) (A = 2–3); II ethyl enol ether (A = 1) (m.p. 180–181°, $[\alpha]_D$ −146° λ_{max} 251 μ, log ε 4.35). Similarly, progesterone, 17α-hydroxyprogesterone caproate and "S" 17,21-diacetate were converted to their respective 6α-chloro derivatives III, IV and V.

Conversion of II to its 1-dehydro analog VI was accomplished by selenium dioxide oxidation.

Treatment of I with N-bromosuccinimide in aqueous buffered acetone yielded 6β-bromo-17α-acetoxyprogesterone (m.p. 178–180°, $[\alpha]_D$ ± 0°, λ_{max} 246 mμ, log ε 4.14) inverted by acid to the α-derivative VII (A = 1). Bromination of 1-dehydro-17α-acetoxyprogesterone[4] with N-bromosuccinimide in carbon tetrachloride gave the 6β-bromo derivative (m.p. 170–172°, $[\alpha]_D$ +23°, λ_{max} 250 mμ, log ε 4.24) inverted by acid to 1-dehydro-6α-bromo-17α-acetoxyprogesterone (VIII) (A = 6).

6-Dehydro-6-chloro-17α-acetoxyprogesterone (IX) and 6-dehydro-6-chloro-"S" diacetate (X) were obtained by chloranil oxidation[5,6] of II and V, while selenium dioxide oxidation of IX and X yielded the 6-chloro-$\Delta^{1,4,6}$-trienones XI and XII.

In multi-dose Clauberg assays[3] it was found that the progestational activity of 6α-chloro-17α-acetoxyprogesterone was increased by Δ^1- or by Δ^6-double bond introduction with the latter modification inducing the more pronounced effect. *The oral progestational activity of IX was 50× that of Norlutin or 700× that of 17α-acetoxyprogesterone and would thus appear to be the most potent*

TABLE I

Compound	M.p. °C.	$[\alpha]_{D\,CHCl_3}$	EtOH max. (mμ)	log ε	Oral progest.[4] activity (Clauberg assay)
17α-Ethynyl-19-nortestosterone					1
17α-Acetoxyprogesterone					0.07
6α-Methyl-17α-acetoxyprogesterone[a,6]					2–3
6-Dehydro-6-methyl-17α-acetoxyprogesterone[6]					12
1-Dehydro-6α-fluoro-17α-acetoxyprogesterone					6
6-Dehydro-6-fluoro-17α-acetoxyprogesterone					15
6α-Chloro-17α-acetoxyprogesterone (II)	polymor. 183–184 215–216	+40°	236	4.20	2–3
6α-Chloroprogesterone (III)	130–132	+133°	237	4.19	
6α-Chloro-17α-hydroxyprogesterone caproate (IV)	Oil	+20°	238	4.15	
1-Dehydro-6α-chloro-17α-acetoxyprogesterone (VI)	203–205	−77°	242	4.21	8
6-Dehydro-6-chloro-17α-acetoxyprogesterone (IX)	212–214	+8°	285	4.36	50
1,6-Bisdehydro-6-chloro-17α-acetoxyprogesterone (XI)	168–170	−83°	229 258 297	4.00 4.00 4.03	35
6α-Chloro-"S" diacetate (V)	197–198	+34°	237	4.19	0.5
6-Dehydro-6-chloro-"S" diacetate (X)	248–250	+37°	285	4.31	1.5
1,6-Bisdehydro-6-chloro-"S" diacetate (XII)	201–203	−36°	228 260 295	4.00 4.03 4.07	1
6α-Bromo-17α-acetoxyprogesterone (VII)	163–166	+42°	236	4.12	1
1-Dehydro-6α-bromo-17α-acetoxyprogesterone (VIII)	172–175	−7°	244	4.15	6

[a] This substance was first described by J. C. Babcock, E. S. Gutsell, M. E. Herr, J. A. Hogg, J. C. Stucki, L. E. Barnes and W. E. Dulin, THIS JOURNAL, **80**, 2904 (1958).

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[1] Paper CXXVI, A Bowers, E. Denot, R. Urquiza and L. M. Sanchez Hidalgo, *Tetrahedron*, in press (1959).

[2] Correct elemental analyses were obtained for all new compounds.

[3] Clauberg assays, by the Endocrine Laboratories. A = oral progestational activity, 17α-ethynyl-19-nortestosterone (Norlutin) = 1.

[4] M.p. 229–230°, $[\alpha]_D$ +19°, λ_{max} 243 mμ, log ε 4.20.

[5] A. J. Agnello and G. Laubach, THIS JOURNAL, **79**, 1257 (1957).

[6] H. J. Ringold, J. Pérez Ruelas, E. Batres and C. Djerassi, *ibid.*, **81**, in press (1959).

progestational agent yet described.[7] The effect of dehydrogenation at C-1 and C-6 was not cumulative (XI, *A* = 35). Inhibition of ovulation in the rabbit with this series of compounds was found to parallel closely the Clauberg assays.

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(7) For the progestational activity of 1- and 6-dehydro-6-methyl-17α-acetoxyprogesterone derivatives, see ref. 6.

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RECEIVED APRIL 30, 1959

FORMATION OF DIBORANE FROM BORONTRICHLORIDE AND MONOSILANE[1]

Sir:

Calculations based on bond energies indicate that the formation of diborane by reaction of silane and trichloroborane should be slightly exothermic. A radical chain process seemed to offer a promising mechanism for achieving hydride transfer. It was subsequently found that mixtures of SiH_4 and BCl_3 do react in the presence of methyl radicals to produce diborane in good yield. Using the photochemical decomposition of azomethane as a source of methyl radicals,[2] the reaction products were found to be diborane, methane and both mono- and dichlorosilane. In addition, a considerable amount of non-volatile substance was produced in the reaction. In a typical experiment 0.19 mmoles of azomethane was decomposed by a 45-minute ultraviolet irradiation in the presence of 4.57 millimoles of SiH_4 and 1.52 millimoles of BCl_3. A 67% yield of diborane (0.51 millimole) was isolated. Reactions thus far have all been carried out at room temperature.

Since methane was among the products and no methyl chloride was observed, it appears that the first step involves the attack of the methyl radical on SiH_4 rather than on BCl_3. It then seems probable that the reaction continues by a radical chain mechanism to the ultimate formation of diborane. The probability of methyl radical attack on SiH_4 was substantiated by noting only partial recovery of silane when mixtures of silane and azomethane were irradiated with ultraviolet light. No attempt has yet been made to identify products of this reaction.

The clear, viscous, non-volatile reaction product was soluble in carbon disulfide and an infrared spectrum showed absorption at 3.9 microns, indicating the presence of boron–hydrogen bonds. Removal of the carbon disulfide left a material soluble in dilute sodium hydroxide, giving a solution which reduced silver nitrate. Prolonged exposure of the original material to air converted it to a water-soluble, white solid.

Experiments are presently being carried out to determine optimum conditions for this reaction. Other radical initiators may be more suitable and will be investigated along with the possibilities of using substituted silanes and other boron halides.

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RECEIVED APRIL 23, 1959

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(1) Contribution No. 881 from the Department of Chemistry, Indiana University.

(2) The photodecomposition of azomethane occurs readily in Pyrex vessels with radiation of wavelength less than 3660 Å. The quantum yield passes through a maximum in the region 3660 to 3350 Å.; *cf.* G. S. Forbes, L. J. Heidt and D. V. Sickman, THIS JOURNAL, **57**, 1935 (1935).

BOOK REVIEWS

Low Temperature Physics and Chemistry. Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry Held at the University of Wisconsin, Madison, Wisconsin, August 26–31, 1957. Edited by JOSEPH R. DILLINGER. The University of Wisconsin Press, 811 State Street, Madison, Wis. 1958. xxv + 676 pp. 16 × 24 cm. Price, $6.00.

The Madison Conference on Low Temperature Physics and Chemistry was attended by four hundred and forty scientists from fourteen different countries. This book contains the essential content of two hundred and twenty-four papers which were presented. It is impressive evidence not only of the recent growth in quantity of low temperature research but also of the increasing variety of experiments now being carried on in the region near Absolute Zero. Such polar explorations have not only uncovered phenomena such as superconductivity and superfluidity exclusively associated with conditions of low thermal energy; but they are also contributing to many other fields ranging from the thermal, magnetic and electric aspects of the solid state to nuclear behavior; even the possibilities of technical applications of low temperature such as superconducting computor elements are being investigated.

This volume will be valuable to many people in many different ways. First, it gives a quick and yet quite comprehensive bird's eye view of the present state of cryogenic research, a perspective which is enhanced by twenty-six invited papers which are presented at greater length than the contributed papers and form a framework about which the latter papers fall naturally into groups.

In the second place, the papers include a number of important ideas and experiments which are opening up really new vistas; in many cases references are given to places where more complete discussion may be found. Finally there are the reports on work which is the continuation of research already in progress for some years. Naturally, the completeness and quality of the papers vary; but the editing is excellent throughout. The process used for printing makes a readable book, although the illustrations are not as clear as in a normal printed text.

Regarding the topics covered, first there are several dozen papers on the experimental and theoretical aspects of superfluidity and superconductivity. A report by Pellam on a superfluid "wind tunnel" is especially intriguing. Chemists may be glad to see the section on temperature scale and measurement which has a bearing on many thermodynamic