ture for 2 hours. It was then concentrated using an air blower. It was filtered and 4 g. (78.5% of theory) of a colorless, crystalline material was obtained. Recrystallized from glacial acetic acid, it melted at 105° (uncor.).

Anal. Calcd. for $C_{12}H_{16}O_3Si$: Si, 11.86. Found: Si, 11.4.

Bis-(cyclopentadienyl)-dimethylsilane (IV).—Half of the above-described cyclopentadienylmagnesium bromide solution was added gradually to a solution of 207 g. of dimethyldichlorosilane in 250 cc. of benzene. The reaction mixture was refluxed for 15.5 hours. It was filtered and the inorganic precipitate washed with benzene. The solvent was removed and the residual material vacuum distilled. The product, a colorless liquid, distilled at 73° at 25 mm. This material gave a negative chlorine test. The yield was about 40%.

*Anal.* Calcd. for $C_{12}H_{16}Si$: Si, 14.89. Found: Si, 14.5.

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The Kinetics of 20-Keto Reduction in 11α-Acetoxypregnane-3,20-dione by Sodium Borohydride

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The selective reduction by sodium borohydride of the 3-keto group of pregnane-3,20-diones to the 3α-hydroxy configuration has been reported.[1-3] In the course of studies on the quantitative rates of selective reduction we have found that the reduction of the 3-keto group of the dione I occurred too rapidly for precise measurement under our experimental conditions. Therefore, we have investigated the kinetics of the reduction of the C-20 carbonyl group. The kinetics of borohydride reduction of 3α-hydroxy-11α-acetoxypregnan-20-one (II) are bimolecular with respect to carbonyl and sodium borohydride concentration. The stoichiometry of the reduction requires one mole of sodium borohydride to four moles of carbonyl.
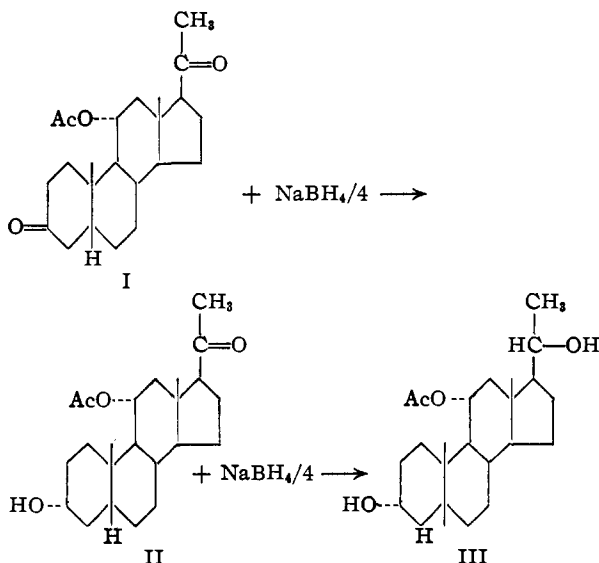
(1) J. A. Hogg, D. A. Lyttle and A. H. Nathan, U. S. Patent 2,647,-134.

(2) O. Mancera, A. Zaffaroni, B. A. Rubin, F. Sondheimer, G. Rosenkranz and C. Djerassi, This Journal, 74, 3711 (1952).

(3) O. Mancera, Howard J. Ringold, C. Djerassi, G. Rosenkranz and F. Sondheimer, *ibid.*, 75, 1286 (1953).

Materials.—The $NaBH_4$ (Metal Hydrides, Inc.) was used as received from the manufacturer. The 11α-acetoxypregnane-11,20-dione[4] melted at 149.5–153.5°. The 3α-hydroxy-11α-acetoxypregnan-20-one[1] melted at 145.5–147.0°. The dioxane was freshly distilled over $NaBH_4$.

Borohydride Assay.—The effective borohydride concentration of the solutions used was determined in the following manner: a 5-cc. sample containing up to 15 mg. of $NaBH_4$ was pipetted into a solution of 1 cc. of 2 N NaOH and 25 cc. of 0.1 N KIO$_3$. To this was added 1 g. of KI, 15 cc. of CHCl$_3$ and 12 cc. of 2 N H$_2$SO$_4$. The released I$_2$ was titrated with 0.1 N Na$_2$S$_2$O$_3$ using 1% starch indicator. The equivalent weight of $NaBH_4$ is $^1/_8$ molecular weight.[5]

Rate Studies.—The ketosteroid was dissolved in dioxane and this solution was added to an aqueous solution of sodium borohydride previously assayed and of known alkalinity. The resulting solvent was 68.5% dioxane. Aliquots were removed at timed intervals and titrated by the procedure given above.

The composition of the solutions studied is given in Table I.

TABLE I

THE REACTION CONDITIONS FOR SODIUM BOROHYDRIDE REDUCTIONS OF KETOSTEROIDS IN 68.5% DIOXANE

Run no.[a]	Temp., °C.	NaBH$_4$, M	NaOH, M	k (l. mole^{-1} hr.$^{-1}$)[b] for 20-ketone reduction
1[c]	15 ± 0.5	0.00656	0.0544	..
2	25.5 ± .3	.0502	.0564	0.40
3	56.0 ± .5	.0533	.0552	3.6
4	57.0 ± 1.0	.0533	.0281	3.7
5	56.0 ± 0.5	.0262	.0555	4.2
6	56.5 ± 0.2	.0389	.0552	3.9

[a] Runs 1 through 5 were with 0.0517 M 11α-acetoxypregnane-3,20-dione (I). Run 6 was with 0.0517 M 3α-hydroxy-11α-acetoxypregnan-20-one (II). [b] The bimolecular rate constant, k, is calculated from the product of 2.303/$(4A - B)$ and the slope of the linear plot of log $[(A - x)/(B - 4x)]$ *vs.* time in hours. The initial carbonyl molarity (B) is twice the molarity of the diketosteroid and equal to the molarity of the monoketosteroid. The initial molarity of borohydride is A and x is the calculated consumption of borohydride at time t. [c] 87% of the $NaBH_4$ was consumed within two minutes.

Results and Discussion

The relatively instantaneous reduction of the 3-keto group of 11α-acetoxypregnane-3,20-dione under the mildest conditions studied is shown in run no. 1 at 15° and with no borohydride in stoichiometric excess of the 3-keto group (Table I). In the other runs the consumption of a second stoichiometric equivalent proceeded at a measurable rate. Each molecule of borohydride was equivalent to the reduction of four carbonyls.

This is consistent with the proposed mechanism of Chaikin and Brown[6] of a 1:4 adduct prior to hydrolysis. On the postulate that this adduct is formed in four successive steps, 1:1, 1:2, 1:3 and finally, 1:4, and that the first 1:1 adduct formation is rate determining, the over-all rate expression is

$$dx/dt = k(A - x)(B - 4x)$$

where A = [$NaBH_4$], the initial molar concentration of sodium borohydride, B = [R_2C=O], the molar concentration of reducible carbonyl groups,

(4) S. H. Eppstein, D. H. Peterson, H. Marian Leigh, H. C. Murray, A. Weintraub, L. M. Reineke and P. D. Meister, *ibid.*, 75, 421 (1953).

(5) D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, 24, 1843 (1952).

(6) S. W. Chaikin and W. G. Brown, This Journal, 71, 122 (1949).

and x = amount of borohydride reacted at time t. This expression may be integrated to

$$\log [(A - x)/(B - 4x)] = (4A - B)kt/2.303 - \log (B/A)$$

The typical bimolecular plot for this equation is given in Fig. 1 for the data of run no. 2. The linearity is consistent with this postulated mechanism which is further substantiated by the fact that variation of the initial borohydride concentration does not significantly affect the rate constant (Table I, runs 3 and 5).
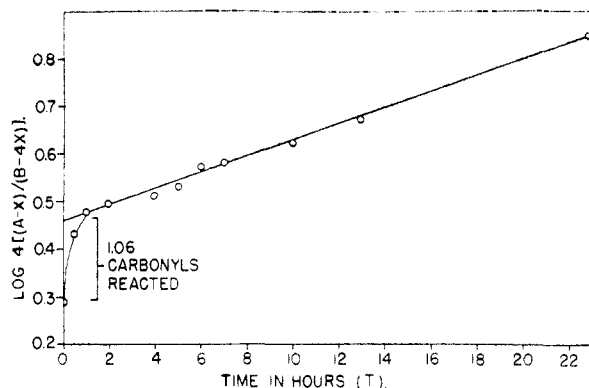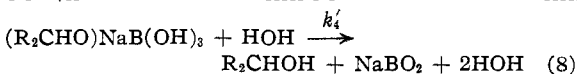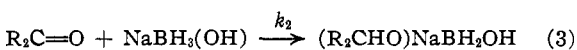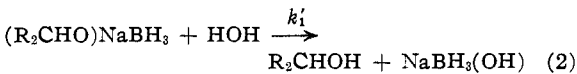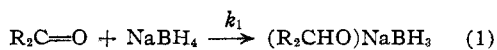

Fig. 1.—Bimolecular plot of log $4[(A - x)/(B - 4x)]$ against time (t) in hours at 25° in 68.5% dioxane for the reduction of the initial reducible carbonyl concentration (B) by the initial sodium borohydride concentration (A), where x is the amount of borohydride reacted at time (t): A = 0.0502 M NaBH$_4$; $B/2$ = 0.0517 M 11α-acetoxypregnane-3,20-dione and the initial solution is 0.0564 M in NaOH.

These kinetics are also consistent with an alternative mechanism, one that does not postulate a large tetrasteroid complex with borohydride in aqueous solution or does not necessitate borohydride–steroid adducts reacting with carbonyls at faster rates than borohydride alone. This alternative mechanism would involve the rate-determining formation of a 1:1 steroid–borohydride complex which undergoes hydrolysis to a corresponding carbinol and an oxidized borohydride moiety. This moiety may subsequently react quickly in non-rate-determining steps with other molecules of carbonyl. The presence of alkali may assist in their stabilization. The sequence of equations may be written

$$R_2C{=}O + NaBH_4 \xrightarrow{k_1} (R_2CHO)NaBH_3 \quad (1)$$

$$(R_2CHO)NaBH_3 + HOH \xrightarrow{k_1'}$$
$$R_2CHOH + NaBH_3(OH) \quad (2)$$

$$R_2C{=}O + NaBH_3(OH) \xrightarrow{k_2} (R_2CHO)NaBH_2OH \quad (3)$$

$$(R_2CHO)NaB(OH)_3 + HOH \xrightarrow{k_4'}$$
$$R_2CHOH + NaBO_2 + 2HOH \quad (8)$$

where the rate constant k_1 (and/or k_1') is very much smaller than the rate constants k_2, k_3, k_4 and the hydrolysis constants k_2', k_3', k_4'.

The wide discrepancy in reactivities of the 3- and 20-keto groups is shown in Fig. 2 for runs no. 3 and 6. The open circles represent the reduction of the

diketo compound, 11α-acetoxypregnane-3,20 dione (I). The solid circles represent the reduction of the monoketo compound, 3α-hydroxy-11α-acetoxypregnan-20-one (II). The conditions at the start of this latter reaction were chosen to be exactly the same as those of the former on the assumption of instantaneous reduction of the 3-keto groups. The agreement of the data with the common line drawn through the points is confirmatory.
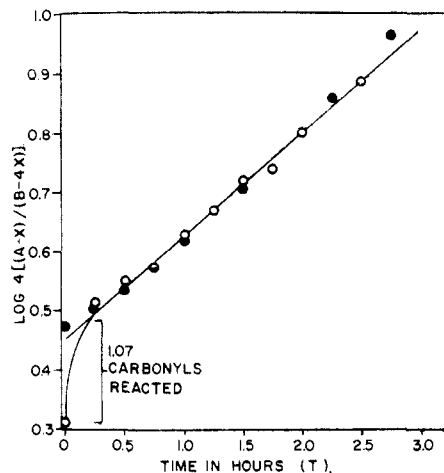

Fig. 2.—Bimolecular plot of log $4[(A - x)/(B - 4x)]$ against time (t) in hours at 56° in 68.5% dioxane for the reduction of the initial carbonyl concentration (B) by the initial sodium borohydride concentration (A), where x is the amount of borohydride reacted at time (t). For the solid circles, A = 0.0389 M NaBH$_4$, B = 0.0517 M 3α-hydroxy-11α-acetoxypregnan-20-one. For the open circles, A = 0.0533 M NaBH$_4$, $B/2$ = 0.0517 M 11α-acetoxypregnane-3,20-dione. Both reaction solutions were initially 0.0552 M in NaOH.

Variation in alkali concentration has no mechanistic effect on the reduction rate as per the rate constants for runs no. 3 and 4. Run no. 4 did show an apparent rate increase near completion of the reduction of the 20-keto group which can readily be accounted for by concomitant decomposition of borohydride in a more acidic media.[5] It is indicated that alkali concentration, above the necessary minimum to stabilize the borohydride, is not kinetically significant.

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Metal–Water Reactions. I. The Reaction between Calcium and Water Vapor*

By Dale S. Gibbs and Harry J. Svec

During the development of an analytical method for determining the oxygen content of Ca metal, the reaction between water vapor and Ca metal was studied. In the temperature range 177 to 369° a series of distinct reactions was found. In order of occurrence these are