order or at different rates. However, the induced exchange was reproducible when conditions were held constant so we were able to correct for it using the equation

$$\% \text{ exchange} = \frac{\% \text{ exchange (measured)} - \% \text{ exchange (induced)}}{100 - \% \text{ exchange (induced)}} (100)$$

The corrected values (always three or more excluding the value at zero time) obeyed the exponential exchange law.[3,4] The half-times for the exchange rates are summarized in Table I. As expected the exchange rate is not dependent on the method of separation when proper account is taken of the induced exchange.

TABLE I

Tl(I)-Tl(III) EXCHANGE RATES
0.0244 f. Tl(I), 0.0244 f. Tl(III)

Acid	Temperature	Method of separation	Exchange, half-time hr.
1.0 f. HNO_3	*ca.* 25°C.	Bromide	2.5 ± 0.2
1.5 f. HNO_3	24.8 ± 0.2°	Bromide	1.8 ± 0.
1.5 f. HNO_3	24.8 ± 0.2°	Hydroxide	1.6 ± 0.2
1.5 f. $HClO_4$	24.8 ± 0.2°	Hydroxide	36 ± 4
1.5 f. $HClO_4$	24.8 ± 0.2°	Bromide	35 ± 4
1.5 f. $HClO_4$	24.8 ± 0.2°	Bromide	33 ± 4
2.5 f. $HClO_4$	24.8 ± 0.2°	Bromide	45 ± 4
3.5 f. $HClO_4$	24.8 ± 0.2°	Bromide	67 ± 5

We are extending this work to determine the effect of temperature, ionic strength, and concentrations of the reactants on the exchange rate.

(3) H. A. C. McKay, *Nature*, **142**, 997 (1938).
(4) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

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RECEIVED DECEMBER 10, 1947

THE STRUCTURE OF THE DECABORANE MOLECULE

Sir:

We are studying the structure of crystalline decaborane, $B_{10}H_{14}$, by single crystal X-ray diffraction methods. We have established the approximate positions of the ten boron atoms and four of the hydrogen atoms, and have assigned probable positions to the remaining ten hydrogen atoms. (Hydrogen atoms are well resolved in fourier sections.)

The $B_{10}H_{14}$ molecule has the symmetry C_{2v}–mm2. The bond distances are as follows (see figure): B_1–B_1', B_1–B_4, B_2–B_3, B_2–B_4, B_3–B_4, are all 1.74 ±0.04 kX; B_1–B_2 and B_4–B_4' are 1.96 ± 0.04 kX; B_4–H_4 is 1.34 ± 0.04 kX,[1] and all other B–H distances are assumed the same, except B_6–H_6 which is assumed to be 1.54 ± 0.04 kX. (B_4–B_4''' and B_4'–B_4'' are 2.76 ± 0.04 kX and are not bond distances.) Each hydrogen atom, except H_6 and H_6' is bound to a single boron atom; H_6 and H_6' are each bound to two boron atoms. Each boron atom has three boron neighbors at 1.74 ± 0.04 kX and one hydrogen neighbor at 1.34 ± 0.04 kX. In addition, B_4, B_4', B_4'' and B_4''' each has a boron neighbor at 1.96 ± 0.04 kX and another hydrogen neighbor at 1.54 ± 0.04 kX; B_1, B_1', B_2, B_2', each has two boron neighbors at 1.96 ± 0.04 kX; B_3 and B_3', each has another hydrogen neighbor at 1.34 ± 0.04 kX.

(1) H_4, H_4', H_4'' and H_4''' were located on an electron density map; the positions of the other hydrogen atoms are assumed.

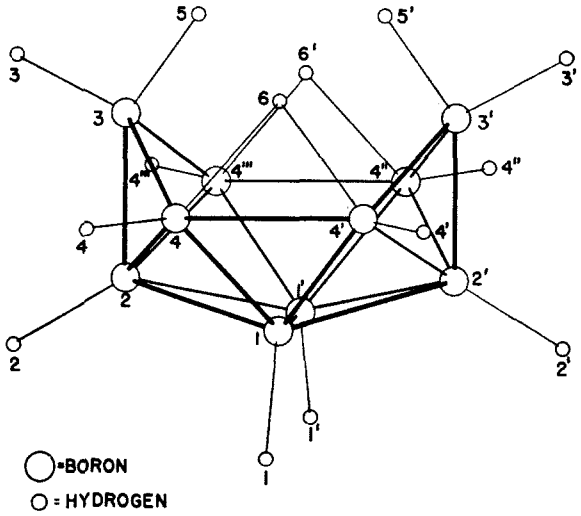

Fig. 1.

Each boron atom is bound to five or six other atoms, but the bonds are not all equivalent. Inasmuch as a bond distance of 1.96 kX has about half the "bond number"[2] of a bond distance of 1.74 kX, one can say that each boron forms five bonds of bond number 0.60. The corresponding radius, R(0.60) = 0.87 kX. Consequently, R(1) = 0.80 kX in agreement with Pauling.[2]

This structure for $B_{10}H_{14}$ gives excellent agreement with the observed X-ray diffraction intensities and also with the electron diffraction observations of S. Bauer.[3]

A detailed discussion of the determination of the structure of crystalline decaborane will be published soon.

(2) L. Pauling, THIS JOURNAL, **69**, 542 (1947).
(3) S. Bauer, *ibid.*, **70**, 115 (1948).

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RECEIVED JANUARY 21, 1948

HETEROGENEITY OF CRYSTALLINE BETA-LACTOGLOBULIN

Sir:

That crystalline β-lactoglobulin is not a homogeneous protein was indicated by the solubility measurements of Grönwall[1] and by the electrophoretic results of Li.[2] Our experiments with

(1) Grönwall, *Compt. rend. trav. lab. Carlsberg*, **24**, no. 8–11, 185 (1942).
(2) Li, THIS JOURNAL, **68**, 2746 (1946).

this protein confirm these reports and indicate a relationship between the solubility of the protein and its composition as defined by the electrophoretic patterns obtained at *p*H 4.7.

β-Lactoglobulin was prepared by the method of Palmer[3] which involves the fractionation of milk whey with ammonium sulfate after the removal of casein with acid. The isolated β-lactoglobulin was recrystallized four times by dialyzing away the salt from sodium chloride solutions at the isoelectric point. Electrophoretic studies on a 1% solution of this material in acetate buffer of ionic strength 0.1, *p*H 4.8, showed the presence of a two component system. The same preparation was electrophoretically homogeneous on the alkaline side of the isoelectric point.

Fractionation experiments on the whey proteins from the filtrate after the partial removal of crystalline β-lactoglobulin gave crystalline fractions with a mobility comparable to that of the usual β-lactoglobulin at *p*H 8.3. Electrophoresis *p*H 4.8, however, indicated a variation in the concentration of the components in each of the fractions. These new crystalline fractions also varied from the standard preparation in that they showed a greater solubility in water and in dilute salt solutions.

Crystallization of the standard preparation by dialysis from an acetate buffer solution, varied with respect to *p*H, gave fractions with a partial separation of the components as indicated electrophoretically. Partial separation of β-lactoglobulin has also been obtained by fractionation with alcohol at low temperatures. The fractions obtained by alcohol have properties in agreement with the data reported in the table below for preparations obtained by the other methods. These results will be reported subsequently.

The solubility experiments were made as described by Grönwall.[1] In every case a suspension of the crystalline material containing 7.6 ± 0.1 mg. protein nitrogen per ml. was equilibrated for a twenty-four hour period. The protein nitrogen was then determined on the supernatant liquid after centrifugation. The table illustrates the variations in the electrophoretic components of a number of preparations at *p*H 4.8 and the solubility of these crystalline fractions at *p*H 5.2 ± 0.1.

Preparation	% Composition, $\mu \times 10^8$ 1.4–1.5	2.2–3.2	Solubility (mg. N/cc.) at 25° in H_2O	in 0.02 *M* NaCl
B[a]	28	72	0.08	1.1
A[a]	38	62	.10	1.3
Standard	40	60	.12	1.5
K[b]	46	54	.18	1.7
L[b]	54	46	.13	1.6
M[b]	59	41	.19	1.9

[a] Preparations made from the standard preparation by means of acetate buffer of varying *p*H. [b] From filtrate of standard β-lactoglobulin preparation.

(3) Palmer, *J. Biol. Chem.*, **104**, 359 (1934).

The variation in solubility in salt solutions of preparations with different electrophoretic compositions is an adequate explanation for the divergent solubility data reported by Palmer[3] and Grönwall.[1]

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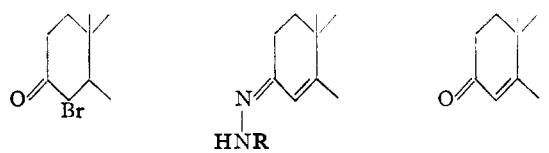
RECEIVED DECEMBER 15, 1947

THE PREPARATION OF 3-KETO-Δ⁴-STEROIDS

Sir:

For the introduction of a double bond at $C_4 : C_5$ in 3-ketosteroids hydrogen bromide has been eliminated from the 4-bromo derivative by treatment in boiling pyridine.[1] However, the yields have not been good. A new method for dehydrobromination has been found in which the reactivity of the bromine at C_4 is greatly increased through formation of a hydrazone at C_3. For a model compound, methyl 3,11-diketo-12-bromocholanate[2] was brominated to give methyl 3,11-diketo-4,12-dibromocholanate (I), m. p. 157.5–158.5°, $[\alpha]_D$ +13 ± 2° (*c* 0.96 in chloroform). Calcd. for $C_{25}H_{36}O_4Br_2$: C, 53.58; H, 6.48; Br, 28.52. Found: C, 53.56; H, 6.69; Br, 28.5.

When 2,4-dinitrophenylhydrazine (1.2 equivalents) in the absence of molecular oxygen was added to an acetic acid solution of I which contained 5 equivalents of sodium acetate, a hydrazone was formed and hydrogen bromide was eliminated to give methyl 3,11-diketo-12-bromo-Δ⁴-cholenate-3-(2,4-dinitrophenylhydrazone) (II). Hydrogen bromide also was eliminated quantitatively without the use of sodium acetate. Red needles, m. p. 238–239°; $\lambda_{max.}$ 387 mμ, log ε 4.48 (chloroform); yield, 82%. Calcd. for $C_{31}H_{39}O_7BrN_4$: C, 56.45; H, 5.96; Br, 12.12. Found: C, 56.21; H, 5.89; Br, 11.93.



I II III

The hydrazone (II) was converted into III by treatment in 20 cc. of chloroform, 30 cc. of pyruvic acid and 2.2 cc. of 2.3 *N* hydrogen bromide in acetic acid at 45°. After two and one-half hours the pyruvic acid 2,4-dinitrophenylhydrazone was removed with aqueous sodium bicarbonate, any C_{24}-carboxyl was esterified and III was separated in about 90% yield. The product was identical with a sample of III prepared by dehydrobromination of I in pyridine, m. p. 190–191°, $[\alpha]_D$ +29 ± 2° (*c* 1.00 in chloroform); $\lambda_{max.}$ 238 mμ, log ε 4.22 (methanol). Calcd. for $C_{25}H_{35}O_4Br$: C,

(1) Adolf Butenandt and Josef Schmidt, *Ber.*, **67**, 1901 (1934).

(2) R. B. Turner, V. R. Mattox, L. L. Engel, B. F. McKenzie and E. C. Kendall, *J. Biol. Chem.*, **166**, 345 (1946).