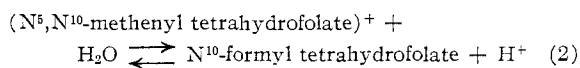


The rate of reaction decreases and increases, respectively, when nitrogen and oxygen are bubbled into a solution of (II).

Following the prolonged interaction of glyoxylate and (I) at pH 4, the product (III) has been purified by precipitation with ethanol and chromatography on columns of powdered Whatman No. 1 paper using 1.0 M formic acid containing 0.1 M mercaptoethanol as the eluent. (III) is easily reduced to (II) by treatment with sodium borohydride under conditions in which N^5, N^{10} -methenyl tetrahydrofolate is also reduced to the N^5, N^{10} -methylene derivative.^{2,3} Hydrolysis of (III) at pH 12 liberated a stoichiometric amount of oxalate, which was isolated as the calcium salt, identified by paper chromatography ($R_f = 0.33$), in phenol: water:98% formic acid (75:25:1), and quantitatively titrated with permanganate.

The rate of conversion of (III) to (IV) at pH 8 is markedly dependent upon the nature of the buffer (phosphate > Tris > maleate); the same order of reactivity in these buffers has been observed previously for the opening of N^5, N^{10} -methenyl tetrahydrofolate to N^{10} -formyl tetrahydrofolate,^{9,10} as shown in equation (2).



(9) S. C. Hartman and J. M. Buchanan, *J. Biol. Chem.*, **234**, 1812 (1959).

(10) H. Tabor and L. Wyngaarden, *ibid.*, **234**, 1830 (1959).

(11) Recipient of the Eli Lilly and Co. Predoctoral Award in the Department of Biochemistry, University of Washington, 1959-1960.

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F. M. HUENNEKENS

RECEIVED OCTOBER 10, 1960

MAGNETIC PHASES OF THE PEROVSKITE TYPE

Sir:

Previous publications from this laboratory have reported the preparation of face-centered cubic phases^{1,2} of composition $A_2^{II}(B^{III}B^V)O_6$ and $A_2^{II}(B^{II}B^{VI})O_6$ which have a structural relationship to the perovskite structure. The bivalent elements A^{II} are large alkaline earth ions in 12-fold coordination with oxygen while the B ions are in octahedral coordination with oxygen. The B ions may be randomly arranged when the combination is trivalent and pentavalent but assume an ordered arrangement when it is bivalent and hexavalent. In the ordered arrangement, each oxygen is shared between a B^{II} and a B^{VI} cation and in the ideal cubic perovskite structure the angle B-O-B is 180°. Such an arrangement of cations is ideal for superexchange between paramagnetic cations. The pairs of B cations which were used previously to obtain ordered perovskite structures have in every case contained only diamagnetic hexavalent or pentavalent ions.

We have prepared recently a series of compounds of this type containing the paramagnetic ion hexavalent rhenium. Examples of these are Ba_2 -

(1) P. Galasso, Lewis Katz and Roland Ward, *THIS JOURNAL*, **81**, 820 (1959).

(2) E. J. Fresia, Lewis Katz and Roland Ward, *ibid.*, **81**, 4783 (1959).

($M^{II}Re^{VI}$) O_6 where $M = Mn, Fe, Co$. Strontium also may be used in place of barium.

Preliminary examination of the physical properties of these substances suggests that they are ferrimagnetic in the case of the compounds containing manganese and iron. The following approximate values are given for the curie temperatures: $Ba_2(Fe Re)O_6$ (40°C), $Ba_2(Mn Re)O_6$ (-137°), $Sr_2(Fe Re)O_6$ (128°). The cobalt compound gave no magnetic response over the temperature range employed. It appears likely that it is antiferromagnetic.

The preparation and characterization of these phases will be described in detail in the near future.

The authors are grateful to Dr. T. J. Swoboda for making the magnetic measurements on these samples.

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ROLAND WARD

JOHN LONGO

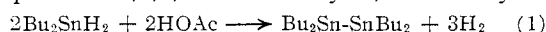
RECEIVED SEPTEMBER 23, 1960

1,2-DIACYLOXYDITINS¹

Sir:

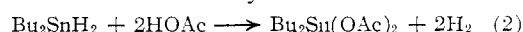
We wish to record the preparation of a new class of organotin compounds, 1,2-diacetyloxyditins.

Di-*n*-butyltin dihydride² (I) (one mole) was found to react with one mole of acetic acid in ether at room temperature according to equation (1) to produce 1,1,2,2-tetra-*n*-butyl-1,2-diacetyloxyditin



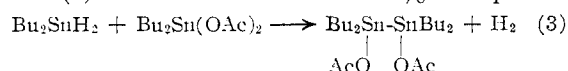
(II) (65% yield), m.p. -7 to -4°, n_D^{20} 1.5060. *Anal.* Calcd. for $C_{20}H_{42}O_4Sn_2$: C, 41.06; H, 7.24; Sn, 40.49. Found: C, 40.81; H, 7.41; Sn, 40.88, 40.80. It reacted with one mole of bromine, giving a product, probably acetoxybromodi-*n*-butyltin (62%), m.p. 67.0-68.5°. *Anal.* Calcd. for $C_{10}H_{21}O_2SnBr$: C, 32.29; H, 5.69; Sn, 31.92; Br, 21.99. Found: C, 32.52; H, 5.71; Sn, 32.21, 31.98; Br, 21.62.

When two moles of acetic acid were used for each mole of hydride the main product was di-*n*-butyltin diacetate formed according to equation (2). With other carboxylic acids also the com-



position of the reaction product mixture depended on the acid/hydride ratio. Ditins were obtained using various carboxylic acids in the yields indicated for analytically pure product: benzoic (65%), *o*-chlorobenzoic (60%), and *p*-chlorobenzoic (16%).

Alternatively, equimolar quantities of I and di-*n*-butyltin diacetate reacted according to equation (3). Gas evolution was 45% complete in



(1) Support of this work by the Office of Ordnance Research, U. S. Army is gratefully acknowledged. Our thanks are also due to Metal and Thermit Corporation for monetary support and gifts of chemicals.

(2) G. J. M. Van Der Kerk, J. C. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 366 (1957).