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 *p*H 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 *p*H 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 *p*H 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).

$$(N^5,N^{10}\text{-methenyl tetrahydrofolate})^+ + H_2O \rightleftharpoons N^{10}\text{-formyl tetrahydrofolate} + H^+ \quad (2)$$

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[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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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 coördination with oxygen while the B ions are in octahedral coördination 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 $Ba_2(M^{II}Re^{VI})O_6$ 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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[1] F. Galasso, Lewis Katz and Roland Ward, THIS JOURNAL, **81**, 820 (1959).

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

DEPARTMENT OF CHEMISTRY ROLAND WARD
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STORRS, CONNECTICUT JOHN LONGO

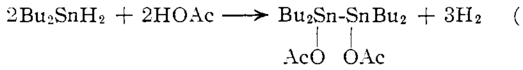
RECEIVED SEPTEMBER 23, 1960

1,2-DIACYLOXYDITINS[1]

Sir:

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

Di-*n*-butyltin dihydride[2] (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-diacetoxyditin



$$2Bu_2SnH_2 + 2HOAc \longrightarrow \underset{AcO\quad OAc}{Bu_2Sn\text{-}SnBu_2} + 3H_2 \quad (1)$$

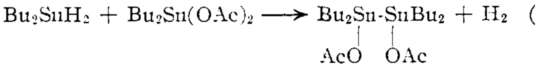
I II

(II) (65% yield), m.p. −7 to −4°, $n^{26}D$ 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 composition 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%).

$$Bu_2SnH_2 + 2HOAc \longrightarrow Bu_2Sn(OAc)_2 + 2H_2 \quad (2)$$

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



$$Bu_2SnH_2 + Bu_2Sn(OAc)_2 \longrightarrow \underset{AcO\quad OAc}{Bu_2Sn\text{-}SnBu_2} + H_2 \quad (3)$$

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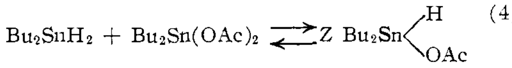
[1] Support of this work by the Office of Ordnance Research, U. S. Army is gratefully acknowledged. Our thanks are also due to Metal and Thermit Corporation for monetary support and gifts of chemicals.

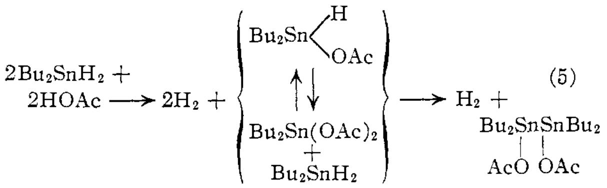
[2] G. J. M. Van Der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 366 (1957).

five hours and, at the end of 18 hours, a compound with properties identical to those of II was isolated in 91% yield. Similarly, reaction between I and di-*n*-butyltin dibenzoate yielded tetra-*n*-butylditin dibenzoate in 48% yield.

Upon mixing di-*n*-butyltin dihydride and di-*n*-butyltin diacetate the infrared spectra showed that, in addition to the Sn–H band of the dihydride at 1835 cm.$^{-1}$, a new band appeared at 1875 cm.$^{-1}$ immediately. The relative intensities of the two bands varied readily with temperature suggesting the establishment of the equilibrium represented by equation (4). If, immediately after its preparation, this mixture was cooled to −70° a solid was formed which, when recrystallized several times from anhydrous ether at −70°, gave a substance whose tin and hydride hydrogen analyses corresponded to those for di-*n*-butylacetoxytin hydride. *Anal.* Calcd. for $C_{10}H_{22}O_2Sn$: Sn, 40.51; hydride H, 0.34. Found: Sn, 40.60, 40.68; hydride H, 0.33. In the reaction of one mole of di-*n*-butyltin dihydride with one mole of acetic acid, after evolution of one mole of hydrogen, a reaction mixture was obtained whose infrared spectrum was similar to that of the mixture obtained on mixing the reactants of equation (4). In both cases the rates of gas evolution and changes in infrared spectra were similar as the mixtures reacted to form ditin and hydrogen. These observations suggest a common pathway for the formation of ditin from both pairs of reactants, hydride–acetate and hydride–acid. The overall process for the hydride–acid reaction may be represented as shown in equation (5).



$$\mathrm{Bu_2SnH_2 + Bu_2Sn(OAc)_2 \rightleftarrows 2\,Bu_2Sn}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OAc}\end{smallmatrix} \qquad (4)$$



$$2\mathrm{Bu_2SnH_2} + 2\mathrm{HOAc} \longrightarrow 2\mathrm{H_2} + \left\{\begin{array}{c} \mathrm{Bu_2Sn}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OAc}\end{smallmatrix} \\ \uparrow\downarrow \\ \mathrm{Bu_2Sn(OAc)_2} \\ + \\ \mathrm{Bu_2SnH_2} \end{array}\right\} \longrightarrow \mathrm{H_2} + \begin{array}{c} \mathrm{Bu_2SnSnBu_2} \\ \mathrm{AcO\quad OAc} \end{array} \qquad (5)$$

When diphenyltin dihydride[3] was used the product isolated was the ditin regardless of whether the acid/hydride ratio was 1.0 or 2.0. With this hydride analytically pure ditins were obtained with these carboxylic acids in the yields indicated: acetic (75%), monochloroacetic (83%), dichloroacetic (75%), trichloroacetic (35%), trifluoroacetic (32%), benzoic (68%), *o*-chlorobenzoic (47%), *o*-hydroxybenzoic (32%), hexanoic (49%), and octanoic (7%).

Another method for the preparation of 1,2-diacyloxyditins is illustrated by the reaction of diphenyltin with benzoyl peroxide to give slightly impure 1,1,2,2-tetraphenyl-1,2-dibenzoyloxyditin (81%), m.p. 172–179°. The analytical sample recrystallized from benzene melted at 184–185°. *Anal.* Calcd. for $C_{38}H_{30}O_4Sn$: C, 57.92; H, 3.84; Sn, 30.12. Found: C, 57.82; H, 3.79; Sn, 30.25, 30.28.

Tetra-*n*-butyldiacyloxyditins show normal melting behavior, whereas the tetraphenyldiacyloxyditins generally melt with decomposition. In the case of 1,1,2,2-tetraphenyl-1,2-diacetoxyditin two of the products formed on melting were found to be stannous acetate and tetraphenyltin.

1,1,2,2-Tetra-*n*-butyl-1,2-diacetoxyditin lost 12% of its ditin content (as revealed by decrease in bromine titer) on exposure to air for one day, whereas 1,1,2,2-tetraphenyl-1,2-diacetoxyditin showed no measurable loss of ditin content over 48 days.

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RECEIVED OCTOBER 3, 1960

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[3] (a) H. G. Kuivila, A. K. Sawyer, and A. G. Armour, *J. Org. Chem.*, in press. (b) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

BOOK REVIEWS

Magnesium and its Alloys. By C. SHELDON ROBERTS, Fairchild Semiconductor Corporation, Palo Alto, California. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y., 1960. xi + 230 pp. 15.5 × 23.5 cm. Price, $9.00.

A primary aim of the book is to relate the properties, characteristics and processing technology of these materials to principles of modern solid-state metals science. The aim is reflected in the organization. Of nine chapters, 1 through 5 are concerned primarily with topics of the metals-science variety: (1) Physical Properties of Magnesium, (2) Alloy Theory and Properties, (3) Magnesium Alloy Systems, (4) The Deformation of Magnesium, (5) Time-Temperature-Dependent Alloy Phenomena. The next three chapters are organized more around problems of processing and applications, attempting at the same time to preserve some continuity with earlier chapters: (6) Casting Alloys and Technology, (7) Wrought Alloys and Technology, (8) Chemical Properties and Applications. The final Chapter 9 on The Extraction and Refining of Magnesium is effectively done and gives useful supplementary background for the balance of the book.

This broad subject is well worth the effort that it must have cost the author who has done a sound job on a difficult assignment. The book is neatly prepared and attractively illustrated. Referencing is detailed and current and there is much value in having brought together the results of numerous investigations at the Metallurgical Laboratory of The Dow Chemical Co., especially those that have never before been published.

The philosophy of the book is clearly in accord with the current and widespread concern over developments in the field of materials science. The result is a good example of how far matters have progressed in blending science and technology in a recognized branch of metallurgy. To use words of the author from the Preface, he has shown that it is possible "to link the two areas in more than a casual manner." Yet it is still evident that the areas are far apart in many places of practical interest.