

with the exception of the cerium and promethium compounds. The good agreement between experimental and calculated lattice constant sustains the earlier observation of a linear relationship between end-member stannates.

TABLE I

Compound	Lattice constant Exptl.	Lattice constant Å. Calcd.	Calcd. density	Beige color of compound
Tb ₂ Sn ₂ O ₇	10.428 ± 0.005	10.430	7.815	Light
Dy ₂ Sn ₂ O ₇	10.389 ± .006	10.401	7.988	Dark
Ho ₂ Sn ₂ O ₇	10.374 ± .004	10.374	8.080	Light
Tm ₂ Sn ₂ O ₇	10.330 ± .003	10.326	8.281	Very light
Lu ₂ Sn ₂ O ₇	10.294 ± .004	10.286	8.515	Very light

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HYDRIDO COMPLEXES OF IRIDIUM

Sir:

While investigating routes to the lower oxidation states of some transition metals, we have obtained a series of compounds which appear to be hydrido complexes of iridium, $[\text{IrH}_n\text{X}_{3-n}\text{L}_3]$ ($n = 1, 2$; $\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{Ph}_3\text{P}$, Ph_3As or Ph_3Sb). The compounds are prepared simply by heating an iridium salt and ligand with an alcohol (or aqueous alcohol), the mono-hydrido complexes readily being formed also at 25°. The latter are apparently related to those described recently^{1,2} since the commencement of the present studies. The new complexes are air-stable, diamagnetic and non-electrolytes, and some of their other properties are summarized in the table.

TABLE I

Compound	Color	M.p., °C. (dec. in vac.)	Infrared spectrum in 2000 cm. ⁻¹ region
$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$	Yellow	256	2200 Deuteride 1580 ^a
$[\text{IrHCl}_2(\text{Ph}_3\text{As})_3]$	Yellow	240	2170
$[\text{IrHCl}_2(\text{Ph}_3\text{Sb})_3]$	Yellow- orange	201	2100
$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]^b$	White	250	2215, 2110 Deuteride 1584, ^a 1515 ^a
$[\text{IrH}_2\text{Br}(\text{Ph}_3\text{P})_3]^b$	White	242	2240, 2090

^a $\nu_{\text{Ir-H}}/\nu_{\text{Ir-D}} = 1.39$ to 1.40 ; calcd., 1.41 . ^b Light sensitive.

Evidence for an Ir-H bond is obtained from infrared spectra: deuteration indicates that the sharp bands observed in the 2000 cm.⁻¹ region are associated with hydrogen vibrations, and their frequency suggests that they derive from $\nu_{\text{Ir-H}}$, by analogy with other hydrido complexes of transition metals.^{1,2,3}

$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$ is best prepared (95% yield) from $(\text{NH}_4)_2\text{IrCl}_6$ and triphenylphosphine (6 moles) in aqueous 2-methoxyethanol at 100°. (Anal. Calcd. for $\text{IrCl}_2\text{P}_3\text{C}_{64}\text{H}_{46}$: Ir, 18.3; Cl, 6.7; P, 8.8; C, 61.7; H, 4.4. Found: Ir, 18.5; Cl, 6.5; P, 9.0; C, 61.2; H, 4.3.) The other mono-

(1) J. Chatt and B. L. Shaw, *Chem. and Ind.*, 931 (1960).

(2) J. Lewis, R. S. Nyholm and G. K. N. Reddy, *ibid.*, 1386 (1960).

(3) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960), and references quoted therein.

hydrido complexes given in the table were obtained under similar conditions or from aqueous ethanol or 2-ethoxyethanol. In these solvents at 25°, $[\text{IrHX}_2\text{L}_3]$ begins to precipitate after a few hours, a yield of 80% being obtained after several days or weeks. Halogen acid also has been detected in these reactions (hydride/acid $\cong 1/1$; cf. ref. 2).

Under more vigorous conditions, by heating $(\text{NH}_4)_2\text{IrCl}_6$ and triphenylphosphine (10-16 moles) in ethylene glycol to 190°, $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ is formed in 87% yield. (Anal. Calcd. for $\text{IrClP}_3\text{C}_{64}\text{H}_{47}$: Ir, 18.9; Cl, 3.5; P, 9.1; C, 63.8; H, 4.7; mol. wt., 1017. Found: Ir, 18.6; Cl, 3.3; P, 9.0; C, 64.3; H, 4.8; mol. wt. in CHCl_3 , 997.) The corresponding bromide is obtained under identical conditions. (Anal. Calcd. for $\text{IrBrP}_3\text{C}_{64}\text{H}_{47}$: Ir, 18.1; Br, 7.5; P, 8.8; C, 61.1; H, 4.5; mol. wt., 1061. Found: Ir, 18.6; Br, 7.6; P, 8.7; C, 61.4; H, 4.4; mol. wt. in CHCl_3 , 1158.) These compounds represent the first dihydrido complexes of iridium, and probably of any metal synthesized under these simple conditions. The dideuterio complex was prepared by refluxing a suspension of $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ in $\text{C}_2\text{H}_5\text{OD}$ for 10 days.

$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ reacts slowly with HCl (in ether) to give $[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$, but the latter is remarkably resistant to acid at 30°. With excess chlorine (in CHCl_3), the dihydride is oxidized to $[\text{IrCl}_4(\text{Ph}_3\text{P})_2]$. Other isomers of each of the hydrides have been found and are being studied.

Experiments are continuing to investigate the role of the solvent in some of these unusual reactions and to examine the reactions and structures of the products. Dr. R. G. Hayter, to whom the author is indebted for valuable suggestions and discussions, has carried out further reductions of some of these compounds with LiAlH_4 and LiAlD_4 , and these will be reported later.

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L. VASKA

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17 α ,21-ISOPROPYLIDENEDIOXY STEROIDS

Sir:

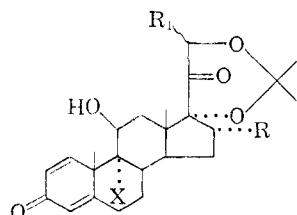
This communication describes the preparation and use of a new protective group for the labile dihydroxyacetone side chain of the corticosteroids. It has been found that cyclic ketal formation occurs readily between the 17 α ,21-diol grouping of the cortical side chain and 2,2-dimethoxypropane in an acid catalyzed exchange reaction to give 17 α ,21-isopropylidenedioxypregnanes in good yields. A solution of 2 g. of prednisolone in 4 ml. of dimethylformamide and 15 ml. of 2,2-dimethoxypropane with 10 mg. of *p*-toluenesulfonic acid was heated for 6 hours to give 1.1 g. of 17 α ,21-isopropylidenedioxy-1,4-pregnadiene-3,20-dione-11 β -ol (I),¹ m.p. 243-247°, $[\alpha]_D +106^\circ$. Other corticoid derivatives prepared had these constants: 17 α ,21-iso-

(1) Satisfactory analyses have been obtained for all new compounds herein described. Ultraviolet absorption spectra are in 95% ethanol. Rotations are in chloroform and melting points are uncorrected. The isopropylidenedioxy derivatives display a characteristic infrared absorption band at 7.25 μ (chloroform).

propylidenedioxy-1,4-pregnadiene-3,11,20-trione, m.p. 201–203°, $[\alpha]_D +214^\circ$; 17 α ,21-isopropylidenedioxy-9 α -fluoro-16 α -methyl-1,4-pregnadiene-3,20-dione-11 β -ol (II), m.p. 263–264°, $[\alpha]_D +83^\circ$; 17 α ,21-isopropylidenedioxy-4-pregnene-3,11,20-trione, m.p. 180–185°, $[\alpha]_D +200^\circ$.

The base stability of the isopropylidenedioxy function makes this blocking group useful in corticosteroid synthesis involving vigorous base catalyzed conditions. Compounds containing the isopropylidenedioxy function are particularly useful for the preparation of modified cortical hormones containing an additional substituent at C-21, which is introduced via the enolate ion derived from the free C-20 ketone.

The acetonide function is removed easily from these blocked steroids by heating at steam bath temperatures with aqueous acetic or formic acids for 1 to 2 hours to regenerate the parent steroid in 50–80% yields.



- I, R = H, R₁ = H, X = H
 II, R = CH₃, R₁ = H, X = F
 III, R = H, R₁ = CH₃, X = H
 IV, R = CH₃, R₁ = CH₃, X = F

A side chain modified cortical hormone containing an additional C-21 methyl group was prepared by treatment of (I) with potassium *t*-butoxide in *tert*-butanol with methyl iodide to yield the 21 ξ -methyl derivative (III), m.p. 245°; $[\alpha]_D +93^\circ$; $\lambda_{\max} 244 \text{ m}\mu$ (13,300). Deacetonation of (III) with 50% acetic acid yielded 21 ξ -methylpredni-

solone which was purified as the 21-acetate, m.p. 218–224°, $[\alpha]_D +97^\circ$; $\lambda_{\max} 244 \text{ m}\mu$ (14,700).²

In a similar manner the side chain homologation of the biologically potent steroid, dexamethasone,³ proceeding through the intermediates (II) and (IV), m.p. 252–258°; $[\alpha]_D +72^\circ$, yielded 21 ξ -methyl dexamethasone,⁴ m.p. 243–246°, $[\alpha]_D +79^\circ$, $\lambda_{\max} 239 \text{ m}\mu$ (15,000).

The biological activity of the 17 α ,21-acetonides of the corticosteroids is of intrinsic interest because of the enhancement of activity in the 16 α -17 α -acetonide of triamcinolone⁵ over the parent steroid. The general utility of the 17 α ,21-isopropylidenedioxy derivatives for the introduction of other substituents at C-21 and for effecting oxidations, halogenations and other base catalyzed transformations with retention of the protective acetonide group will be the subject of a forthcoming publication.

Acknowledgment.—We are indebted to the Schering Corporation for generous financial support of this work.

(2) The physical constants are in agreement with the 21B series reported in a recent publication describing an alternative synthesis of this compound; see E. J. Agnello, R. Pinson, Jr., S. K. Figdor, G. M. K. Hughes, H. W. Ordway, B. M. Bloom and G. D. Laubach, *Experientia*, **16**, 357 (1960).

(3) G. Arth, O. Johnston, J. Fried, W. Spooner, D. Hoff and L. Sarett, *J. Am. Chem. Soc.*, **80**, 3160 (1958); E. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gerbert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman and M. M. Pechet, *ibid.*, **80**, 4431 (1958).

(4) The biological activity of the C-21-methylated compounds in general showed a reduced order (10–30%) of anti-inflammatory activity over the parent unmethylated steroid. We thank Dr. S. Tolksdorf of the Schering Corporation for this information in advance of publication.

(5) J. Fried, A. Borman, W. B. Kessler, P. Grabowich and E. F. Sabo, *J. Am. Chem. Soc.*, **80**, 2338 (1958).

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BOOK REVIEWS

Non-Crystalline Solids. Conference on Non-crystalline Solids, Alfred, New York, September 3–5, 1958. Sponsored by National Academy of Sciences–National Research Council and Air Force Office of Scientific Research, Air Research and Development Command. V. D. FRÉCHETTE Editor, State University of New York College of Ceramics at Alfred University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. xviii + 536 pp. 16 × 23.5 cm. Price, \$15.00.

This book consists of a compilation of twenty papers and discussions representing the proceedings of a conference which brought together leading investigators from several fields for the purpose of clarifying the status of their knowledge and understanding of non-crystalline solids.

The first five chapters deal with scattering of radiation by non-crystalline materials. Electronic structure is treated in chapters 6 to 8. Relaxation phenomena are dealt with in chapters 9 through 12. The final eight chapters are concerned with the structure and properties of special systems. The chapter headings and their authors are:

1. Scattering of Radiation by Non-crystalline Media, P. Debye

2. Spherically Symmetric Fourier Transforms and Medium Range Radial Distribution Functions in the X-Ray Determination of Complex Molecular Structures, D. P. Riley

3. Electron Diffraction Techniques for the Study of Amorphous Systems, S. H. Bauer

4. Structure of Vitreous Silica by Total Neutron Scattering, R. M. Dalaney and A. H. Weber

5. High Temperature X-Ray Diffraction Methods Applied to the Study of Non-crystalline Media. Structure of Molten Fluorides and Chlorides, Jerzy Zarzycki

6. Electronic Band Structure of One-dimensional Disordered Arrays, M. Lax and H. L. Frisch

7. X-Ray Absorption Edge Spectroscopy of Compounds of Chromium, Manganese, and Cobalt in Crystalline and Non-crystalline Systems, Robert A. Van Nordstrand

8. Magnetic Resonance Studies of Glasses, W. P. Slichter

9. The Use and Limitations of Irreversible Thermodynamics in the Study of Relaxation Processes, R. O. Davies

10. Liquid Relaxation Phenomena and the Glass State, Theodore A. Litovitz