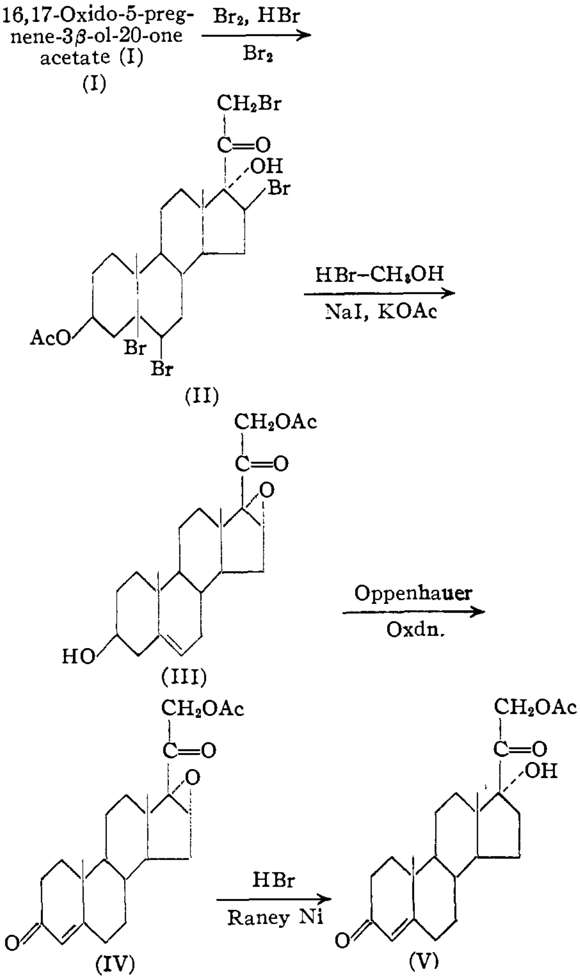
similar to that given IV produced 17α-hydroxyprogesterone.



The smooth cleavage of the oxido compounds by hydrogen bromide, the clean reductive removal of bromine from the resulting bromohydrins by Raney nickel, and the good yields encountered at every step make these hitherto difficultly accessible cortical hormones readily available.

16,17-Oxido-5-pregnene-3β,21-diol-20-one 21-Acetate (III).—From 16,17-oxido-5-pregnene-3β-ol-20-one acetate by treating first with one molar equivalent of bromine in acetic acid–carbon tetrachloride, then with hydrogen bromide in acetic acid followed by a second molar equivalent of bromine. Then hydrolysis with hydrogen bromide in methanol–benzene, treatment with sodium iodide in benzene–ethanol and finally with potassium acetate in acetone gave needles from acetone–petroleum ether, m. p. 190–192°; $[\alpha]^{24}D$ +15° (chloroform). *Anal.* Calcd. for $C_{23}H_{32}O_5$: C, 71.11; H, 8.30. Found: C, 70.86; H, 8.33.

16,17-Oxido-4-pregnene-21-ol-3,20-dione Acetate (IV).—By the Oppenauer oxidation of III; prisms from ether–petroleum ether, m. p. 170–172°; $[\alpha]^{25}D$ +167° (chloroform). *Anal.* Calcd. for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82. Found: C, 71.82; H, 8.23.

17α-Hydroxy-11-desoxycorticosterone Acetate (V).—From IV with hydrogen bromide in acetic acid, followed by reduction with Raney nickel in ethanol; needles from methanol, m. p. 235–238° (sinters 230°), no depression with material isolated from a natural source[2]; $[\alpha]^{24}D$ +114° (acetone). *Anal.* Calcd. for $C_{23}H_{32}O_5$: C, 71.11; H, 8.30. Found: C, 70.94; H, 8.28.

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(2) We are indebted to Dr. Marvin H. Kuizenga of The Upjohn Laboratories for a sample of this material.

THE GLIDDEN COMPANY
RESEARCH LABORATORIES
SOYA PRODUCTS DIVISION
CHICAGO 39, ILLINOIS
PERCY L. JULIAN
EDWIN W. MEYER
WILLIAM J. KARPEL
ISABELLE RYDEN

RECEIVED AUGUST 22, 1949

ELECTRON DEFICIENT COMPOUNDS. IV. THE STRUCTURE OF HEXAMETHYLDIPLATINUM

Sir:

The reaction $(CH_3)_3PtI + K$ was presumed to yield $(CH_3)_3Pt—Pt(CH_3)_3$.[1] A recent explanation of electron deficient bonding[2] suggests that since Pt^{IV} has six low energy orbitals, d^2sp^3, the configuration about platinum should be octahedral, requiring polymerization through electron deficient bonds.

"Hexamethyldiplatinum" is monoclinic, a_0 = 17.35, b_0 = 18.99, c_0 = 17.79 kX., β = 116°, space group from Weissenberg diagrams, $P2_1/c$. The observed density, 3.65, requires 48 $Pt(CH_3)_3$ per unit cell. There can be only 2 or 4 crystallographically equivalent atomic aggregates per unit cell. In molecular crystals these aggregates are almost invariably the molecules, so that the unit cell and density data indicate a minimum molecular size of $[(CH_3)_3Pt]_{12}$. Our data do not exclude continuous chains.

Patterson functions, $P(x,z)$ and $P(x,y)$, have been calculated, each involving about 125 reflections. All important peaks of $P(x,z)$ (Fig. 1) are interpreted, even as to heights, in terms of 16 platinum positions. Since h is even except for 13 weak reflections, there is a pseudo eightfold set of positions: x,z; $\bar{x},\bar{z}$; $x,{}^1/_2 + z$; $\bar{x},{}^1/_2 - z$; ${}^1/_2 + x,z$; ${}^1/_2 - x,\bar{z}$; ${}^1/_2 + x,{}^1/_2 + z$; ${}^1/_2 - x,{}^1/_2 -$

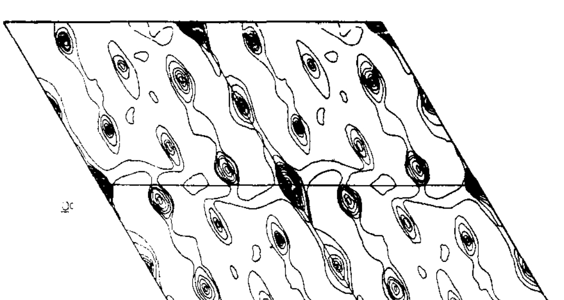

Fig. 1.—Patterson projection, $P(xz)$ for "Hexamethyldiplatinum."

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(1) H. Gilman and W. Lichtenwalter, THIS JOURNAL, **61**, 957 (1939).

(2) R. Rundle, *ibid.*, **69**, 1327 (1947); *J. Chem. Phys.*, **17**, 671 (1949).

z. There are two such sets with $x_1 = 0.313$, $z_1 = 0.125$; $x_2 = 0.138$, $z_2 = 0.008$. These parameters lead to satisfactory $(h0l)$ intensities.

The sixteen platinum positions projected onto (010) form four, well-separated squares per unit with Pt–Pt = 2.84 kX. Each point must represent three platinum atoms. $P(xy)$ gives 2.82 kX. for one important Pt–Pt distance along b_0. There are four molecules, or possibly four continuous chains, per unit cell. The square projection on $P(x,z)$ suggests that platinum is octahedral, as expected. The complete structure has not yet been determined.

"Hexamethyldiplatinum" is quite soluble in benzene, but negligibly soluble in non-aromatic hydrocarbons. The pronounced difference suggests that benzene may depolymerize the molecule. It is noteworthy that benzene leaves the tetramethylplatinum tetramer unaltered.[3]

Thanks are due Prof. Henry Gilman for advice and encouragement.

[3] R. E. Rundle and E. J. Holman, THIS JOURNAL, **71**, 3264 (1949).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
GABRIELLO ILLUMINATI
R. E. RUNDLE

RECEIVED AUGUST 15, 1949

NEW BOOKS

Aquametry. Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water. By JOHN MITCHELL, JR., M.S., and DONALD MILTON SMITH, Ph.D., Ammonia Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. (Chemical Analysis. Vol. V. A Series of Monographs on Analytical Chemistry and Its Applications. Editors: Beverly L. Clarke and I. M. Kolthoff) Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y. 1948. xi + 444 pp. 51 figures. 15.5 × 23.5 cm. Price, $8.00.

The monograph "Aquametry" by John Mitchell, Jr., and Donald Milton Smith is the fifth of a series dealing with topics in Analytical Chemistry. The present work is primarily concerned with "the application of the Karl Fischer reagent to quantitative analyses involving water" but the authors have done much more than is indicated in this sub-title. The book is written in two parts; the first and longer section deals with considerations of a general nature as well as with specific quantitative determinations using the Karl Fischer reagent; the latter part deals with the determination of organic functional groups.

Contained in the first part is a brief survey of the classical methods used for the determination of water. It is shown later that in most cases the Karl Fischer Reagent yields better results and for this reason the older methods are not discussed in detail. There follows a chapter which presents almost in outline form a summary of the most important procedures which utilize the Karl Fischer Reagent. The presentation of this laboratory manual so early in the running text is a departure from the usual practise. It is placed in its particular position so that persons who have studied the pertinent portions of the book will be able to work in the laboratory more efficiently. The authors then present a discussion of possible alternative compositions of the reagent and give what they consider to be the best of those studied. After an investigation of the stoichiometry of the reactions involved, there is given a series of general discussions which deal with the determination of water on the macro and micro scales. This includes an excellent review of the important instrumental as well as the usual visual methods. Then actual working procedures are given for many common organic and inorganic materials. In each of these latter cases there are outlined alternative methods when such exist but these are necessarily brief. Extensive references are given in all cases. The first section is closed with examples of reactions with inorganic compounds which lead to apparent anomalies. These include redox couples which react with the iodine liberated in the titration to give false end-points. The second part of the book will probably be of great use to organic chemists. In this section there are detailed instructions for the determination of various functional groups such as the alcoholic hydroxyl, the amino and the carbonyl radicals. These are not direct titration methods but include some intermediate water producing step. The frequent reference to interfering substances will be of great help to future workers. The book closes with a chapter on work which is as yet not done.

The volume as a whole is formulated in a concise, accurate and readable manner. The lack of serious errors is commendable and is probably due in large part to the care with which practically every entry was checked in the laboratory of the authors. If all future volumes in the Analytical Chemistry series are up to the standards set by Mitchell and Smith, one can easily visualize a set of these treatises in every complete chemical library.

EDWARD H. DE BUTTS

Natural Products Related to Phenanthrene. By LOUIS F. FIESER and MARY FIESER, Department of Chemistry, Harvard University. Third Edition of the Monograph Previously Entitled "Chemistry of Natural Products Related to Phenanthrene" by L. F. Fieser. A. C. S. Monograph No. 70. Reinhold Publishing Corporation, 330 West 42nd Street, New York 18, N. Y., 1949. xii + 704 pp. Price, $10.00.

More than a decade has passed since the scientific world greeted with unanimous acclaim the first edition of Fieser's treatise which Butenandt has called a model *par excellence* for chemical monographs. The first edition arrived at a time when steroid chemistry had just firmly established itself as a special branch of organic chemistry, when most of the important hormones and related products had been discovered and the rough outlines of their structures had been drawn. Since then, in a bewildering multitude of papers, the more intimate structural details have been furnished with which to complete the picture. Once again Fieser, now in coöperation with Mrs. Fieser and Dr. Turner, has summarized the significant developments and has presented them in an eminently lucid and readable manner. The book is much more than a mere review of the subject. It abounds in original ideas concerning the revision of nomenclature, the relations between physical properties and structure of steroids, the course of certain