osmium hexafluoride and iridium hexafluoride.[7]

Table I summarizes some of the properties of the 4d series hexafluorides. The volatility decreases rapidly in going across the series, although each compound is less volatile than its counterpart in the 5d transition series. The solid–solid transition temperatures and the triple points increase regularly; the values given in the table for RhF_6 are approximate extrapolations and have not been observed directly. An attempt to measure the triple point by warming the solid in a glass capillary was unsuccessful because of rapid decomposition of the sample. The infrared active fundamentals ν_3 and ν_4 observed in this series are of the same magnitude as those in the 5d series.[8] Although the metal to fluorine distances are not known for the 4d series, the fact that the infrared frequencies do not vary greatly from molybdenum to rhodium indicates that the metal to fluorine bond lengths also do not vary, as has been found for the 5d series.[8]

TABLE I

	MoF_6	TcF_6	RuF_6	RhF_6
Vapor pressure at 15°	361[a]	135[d]	58[f]	38
Solid-solid transition temp.	−9.55[b]	−5.3[e]	+2.5[f]	(+7)
Triple point	17.45[b]	37[e]	54[f]	(70)
Infrared active fundamental ν_3[c]	741	745	735	722
fundamental ν_4[c]	264	265	275	283.5

[a] O. Ruff and E. Ascher, *Z. anorg. Chem.*, **196**, 419 (1931). [b] A. P. Brady, O. E. Myers and J. D. Clauss, *J. Phys. Chem.*, **64**, 588 (1960). [c] Unpublished results from this laboratory. [d] H. Selig, C. L. Chernick and J. G. Malm, *J. Inorg. Nucl. Chem.*, in press. [e] J. G. Malm and H. Selig, to be published. [f] Ref. 2.

(7) H. H. Claassen and B. Weinstock, *J. Chem. Phys.*, **33**, 436 (1960).
(8) H. H. Claassen, *ibid.*, **30**, 968 (1959).

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STEREOCHEMICAL CONSEQUENCES OF KETONE REDUCTIONS BY DIBORANE AND SUBSTITUTED BORANES

Sir:

We wish to report the achievement of steric control of the reduction of cyclanones by the use of dialkylboranes containing bulky substituents, such as disiamylborane and diisopinocamphenylborane, as well as the applicability of the latter reagent for the asymmetric reduction of ketones.

The reduction of norcamphor by lithium aluminum hydride and by sodium borohydride yields *endo*-norborneol predominantly, evidently produced via a hydride transfer from the reagent to the carbonyl group from the less hindered direction. Similar results are observed in related rigid bicyclic systems.[1] On the other hand, the reduction of 2-methylcyclopentanone and 2-methylcyclohexanone by these reagents gives predominantly (69–75%) of the more stable *trans* alcohol.[2] These phenomena have been discussed by Dauben and his co-workers[2c] in terms of "steric approach control" and "product development control."

Diborane is an interesting reducing agent with reducing capabilities quite different from those of the basic complex hydrides.[3] However, in the present instance it yields predominantly *trans*-2-methylcyclopentanol (69%) and *trans*-2-methylcyclohexanol (65%). The introduction of bulky substituents, as in disiamylborane, markedly modifies the hydroborating[4] and reducing[5] action of the reagent. This reagent led to the predominant formation of the *cis* alcohols: 78% *cis*-2-methylcyclopentanol and 77% *cis*-2-methylcyclohexanol.

In seeking to enhance the steric requirements of the reagents, we had recourse to diisopinocamphenylborane, previously utilized for the asymmetric hydroboration of olefins.[6] With this reagent we realized the formation of 94% *cis*-2-methylcyclopentanol and 92% of *cis*-2-methylcyclohexanol Thus, it has been possible to achieve a shift from predominant *trans* to nearly complete *cis* formation by the use of boranes with high steric requirements.

Diisopinocamphenylborane had led previously to the asymmetric synthesis of alcohols *via* the hydroboration of olefins in optical purities of 80–90%.[6] It was of interest to examine the optical purities of the products resulting from the reduction of ketones with this reagent.

The mixture of 2-methylcyclohexanols exhibited optical activity, but because of the difficulty in separating the two isomers we were unable to determine the optical purities of the individual compounds. Accordingly, we treated a series of methyl ketones, $RCOCH_3$, with this reagent with these results ($[\alpha]^{25}D$, optical purity in %, configuration): R = ethyl, −1.5°, 11%, R; isopropyl, −0.91°, 17%, R; *t*-butyl-, +2.3°, 30%, S[7]; phenyl, +6.0°, 14%, R.

Although the optical purities are far less than those realized in the earlier hydroboration of olefins,[6] they are comparable with those obtained by existing methods. A detailed study of the utility of diisopinocampheylborane for the prediction of absolute configuration is in process.[8]

In a typical reduction a solution of 11.2 g., 100 mmoles, of 2-methylcyclohexanone in 25 ml. of diglyme was added during 15 minutes to a stirred suspension of 100 mmoles of diisopinocamphenylborane[6] in 200 ml. of diglyme. The reaction mixture was stirred at 0° for three hours and then left overnight at room temperature. Following oxi-

(1) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).

(2) (a) J. B. Umland and M. I. Jefraim, *J. Am. Chem. Soc.*, **78**, 2788 (1956); (b) J. B. Umland and B. W. Williams, *J. Org. Chem.*, **21**, 1302 (1956); (c) W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956); (d) W. G. Dauben and R. E. Bozak, *J. Org. Chem.*, **24**, 1596 (1959).
(3) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).
(4) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).
(5) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).
(6) H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).
(7) J. A. Mills and W. Klyne, "The Correlation of Configuration," Chapt. 5 in W. Klyne, ed., "Progress in Stereochemistry," Vol. I, Butterworths Scientific Publications, London, 1954, p. 206, have indicated that the evidence for the assignment of configuration to pinacolyl alcohol "is not entirely convincing."
(8) Research in progress with G. Zweifel and N. R. Ayyangar.

dation with 30 ml. of 3 *N* sodium hydroxide and 30 ml. of 30% hydrogen peroxide, there was isolated 9.62 g. (85% yield) of 2-methylcyclohexanol, b.p. 165°, $n^{20}D$ 1.4643, $[\alpha]^{25}D$ −0.5°. Analysis by gas chromatography (glycerol column at 75°) showed 92% *cis*-, 8% *trans*-2-methylcyclohexanol.

Similar treatment of 10.0 g., 100 mmoles, of pinacolone yielded 8.6 g. (85%) of pinacolyl alcohol, b.p. 119–120°, $n^{20}D$ 1.4154, $[\alpha]^{20}D$ + 2.3°; acid phthalate m.p. 85–86°, $[\alpha]^{20}$ + 18.9° (*c* 3.65 in $CHCl_3$).[9]

(9) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 1120 (1914), reported b.p. 119–120°, $n^{22}D$ 1.4146, $[\alpha]^{20}D$ +7.71°; acid phthalate m.p. 86–87°, $[\alpha]D$ +63.9° (in $CHCl_3$).

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BOOK REVIEWS

Cholesterol. By DAVID KRITCHEVSKY, Associate Member, The Wistar Institute, Assistant Professor of Biochemistry in Medicine, The University of Pennsylvania. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1958. xi + 291 pp. 15.5 × 23.5 cm. Price, $9.75.

Dr. David Kritchevsky's book is a comprehensive review of the chemistry, biosynthesis, biological function and analysis of cholesterol. For the worker in the field it is both a synthesis and a work of reference. For the newcomer, whether he be a chemist or a biologist, it is a stimulating introduction to the knowledge of this important natural substance.

In Chapter 1, Chemistry of Cholesterol, a brief historical review leads to a well presented description of the proof of structure. The evolution and development of chemical reactions now standard and familiar in steroid chemistry are well presented as tools used in nuclear configuration analysis, total synthesis and in methods of preparing cholesterol labeled with the isotopes of hydrogen and carbon. The lability of radioactive cholesterol on storage is described. In Chapter 2, the Biosynthesis of Cholesterol is presented starting with the early balance studies which demonstrated 'in vivo' synthesis and dealing finally with the investigations of enzyme systems obtained from tissue homogenate fractions. The synthesis of cholesterol from acetate *via* squalene, the distribution of acetate carbons in the molecule, the effect of metal ions and dietary factors and the importance of the liver are discussed in an integrated fashion calculated to enhance further research.

Chapter 3 on Absorption and Transport of Cholesterol emphasizes the methods and pitfalls encountered in such studies. The roles of fat, bile acids and cholesterol esterase activity are discussed in relation to absorption of cholesterol into the lymph from the small intestine. The relation of lipoproteins to cholesterol transport in the blood is introduced to lay the foundation for the later discussion (Chapter 5) of their role in cholesterol metabolism in disease states.

Aspects of cholesterol metabolism in relation to body function are discussed in chapter 4. These include its possible role in the transport of fatty acids, as a precursor of steroid hormones and bile acids, as a structural unit in nerve tissue and its antihemolytic properties in plasma. A brief but pertinent discussion on cholesterol balance studies is included. In Chapter 5, Cholesterol in Disease States, the relationship of cholesterol to cancer and to atherosclerosis are discussed in detail. As the layers of complexities are revealed it is obvious that the final answers to the unsolved problems of cancer and circulatory disease can come only through further patient research.

A worker in the field has only to read Chapter 6 on Blood Cholesterol to realize how well Dr. Kritchevsky has summarized and evaluated the pertinent points of the 546 references given at its end. The effects of various diets, of steroid and other hormones and other factors on the equilibria between cholesterol and its esters in blood and in tissues and on their distribution between blood and organs are discussed with special reference to disease states, particularly atherosclerosis. Hypocholesterolemic agents such as 2-phenylbutyric acid, nicotinic acid and plant sterols are considered here.

The last chapter (7), Analysis of Cholesterol, reviews not only the standard and newer analytical methods but also the factors to be evaluated for a given application. The mechanism of sulfuric acid-induced color reactions is discussed. A worthwhile presentation of the merits of column and paper chromatographic methods for cholesterol and its derivatives is included.

An appendix contains physical constants of cholesterol, related sterols and derivatives as well as tables of the cholesterol contents of various foods and tissues. An amazing total of 2092 references covering the literature to 1958 has been used by Dr. Kritchevsky in the compilation of this book which can only be highly recommended.

Some errors, apparently printers', have been noticed. Wislicenus' name is spelled wrong on page 1; on page 11 the structural formula, XXI, for calciferol methyl ether has its C-4 labeled wrong and its double bond missing between C-5 and C-6; on page 40 a double bond should be present between C-5 and C-6 in formula CLXII.

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Comprehensive Analytical Chemistry. Volume IB. Classical Analysis. Edited by CECIL L. WILSON, Ph.D., D.Sc., F.R.I.C., F.I.C.I., Professor of Analytical Chemistry, The Queen's University of Belfast, and DAVID W. WILSON, M.Sc., F.R.I.C., Principal Lecturer, Sir John Cass College, London. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1960. xxii + 878 pp. 16 × 23 cm. Price, $30.00.

"Comprehensive Analytical Chemistry" eventually will comprise five volumes, some volumes consisting of several parts. The aim of the editors as stated in the preface is "to provide a work which in many instances should be a self-sufficient reference work, but where this is not possible it should at least be a natural starting point for any analytical investigation." This book, which is the second part of Vol. I, "Classical Analysis," deals with classical methods of inorganic titrimetric analysis (visual end-point detection) and with organic quantitative analysis. It is written by sixteen specialists, most of whom are from England.

Nearly 400 pages are devoted to inorganic titrimetric methods, of which a chapter "Theory and Practice" by E. Bishop occupies 180 pages. This consists of a clear and somewhat detailed treatment of *p*H and similar calculations appropriate to titrimetric processes, and includes 33 pages of tables of equilibrium constants and electrode potentials. In general the treatment is excellent, aside from the curious statement (p. 11) *re* the effect of ionic strength on equilibrium calculations: "at the equivalence point of titrimetric reactions the concentrations are usually of the order of 10^{-5} *M* or less, when the activities approach unity." A brief chapter on apparatus describes the common types of volumetric glassware and gives practical suggestions on its use. It is of interest to learn (p. 186) that specifications established for the manufacture of titrimetric glassware en-