TABLE III

| Temp., °K. | $\Delta S$[5] Equilib. data | $\Delta S$ 3rd law | $\Delta S$ Free rot. | $\Delta S$ Rest. rot. |
|---|---|---|---|---|
| 457 | 27.44 | 28.39 | 25.34 | 28.39 |
| 475 | 27.56 | 28.37 | 25.40 | 28.37 |
| 491 | 27.73 | 28.35 | 25.47 | 28.35 |

$\Delta H°_{355} = 13{,}400$ cal.[6]

*culated using free rotation and the third law entropies, since the equilibrium data show the latter to be correct.*

Kemp and Pitzer have demonstrated this for ethane and courageously predicted the discrepancies in other cases. *We agree with these authors that there is no reason to doubt the practical applicability of the Third Law.*

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(5) Parks and Kelley, *J. Phys. Chem.*, **32**, 734 (1928).

(6) We wish to thank Professor G. B. Kistiakowsky for advance notice on this recently published value.

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
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RECEIVED FEBRUARY 23, 1938

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## HYDROGEN FLUORIDE AS A CONDENSING AGENT

*Sir:*

We have found that anhydrous hydrogen fluoride will promote the reaction between either olefins and benzene or aliphatic halides and benzene. The following reactions have been accomplished and others are in progress. We are continuing the work with other aromatic compounds.

All reactions were run in the liquid phase at 0° with stirring. The time required varied from two to twenty-four hours. Varying amounts of hydrogen fluoride were used without changing the results.

1. From the reaction of propylene and benzene two products were isolated. The one present in larger amount boiled at 149–150° at 730 mm., and gave an acetamino derivative that melted at 105–105.5°. Isopropylbenzene boils at 152° at 758 mm. and its acetamino derivative melts at 106°.

2. Isopropyl chloride gave indications of a reaction. Some material that boiled above 150° was produced. This formed an acetamino derivative, m. p. 166°, which may be the derivative of diisopropylbenzene.

3. Isobutylene formed two products. One was a liquid, b. p. 166.5–168° at 728 mm., the other was a crystalline solid, m. p. 77–78°. *t*-Butylbenzene boils at 168–170° at 760 mm. and di-*t*-butylbenzene melts at 78°.

4. *t*-Butyl chloride gave two products; one a liquid, b. p. 167–170°, and the other a solid, m. p. 77°. A mixed melting point of this solid and that formed in (3) was 76.5–77.5°. An acetamino derivative of the liquid melted at 169–170°. A dinitro derivative of the solid melted at 188°. The known acetamino derivative of *t*-butylbenzene melts at 170° and the dinitro derivative of di-*t*-butylbenzene melts at 191°.

5. Trimethylethylene formed two products, b. p. 188° and 262–265°.

6. *t*-Amyl chloride formed the same two products that were found in the reaction of trimethylethylene.

DEPARTMENT OF CHEMISTRY
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STATE COLLEGE, PENNSYLVANIA
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RECEIVED MARCH 8, 1938

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## THE PREPARATION AND PHOTOCHEMICAL OXIDATION OF 2,4-CHOLESTADIENE

*Sir:*

A further study of the method of preparation of 2,4-cholestadiene [H. E. Staveley and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937)] indicates that for consistent results it is desirable to use alumina which has been freshly reactivated by heating in a shallow pan at 200° for four hours. Activated Alumina, Grade A, 40 to 80 mesh (Aluminum Ore Co., East St. Louis, Ill.) is suitable. It is convenient to carry out the reaction in a small Pyrex retort. The preliminary heating should be continued for at least thirty minutes beyond the time when the droplets refluxing from the sides fail to crystallize when cooled locally by a jet of compressed air. Subsequent distillation yields 60 to 70% of a product having a specific rotation +90–100°. Distillation at higher temperatures (higher pressures) than previously recommended leads to the formation of cholesterilene, m. p. 79.5–80°, $[\alpha]^{20}_{D}$ −51.4° in ether.

The isolation and purification of the 2,4-cholestadiene has been achieved by systematic fractional recrystallization from small amounts of ether. This is carried out in centrifugal filtration tubes [E. L. Skau, *J. Phys. Chem.*, **33**, 951 (1929); E. L. Skau and L. F. Rowe, *Ind. Eng. Chem., Anal. Ed.*, **3**, 147 (1931)] the yields being kept high by centrifuging at −78°. By this means a pure product is obtained, m. p. 68.5°, $[\alpha]^{23}_{D}$ + 168.5° in ether (30% yield from cholesterol). Comparison of the absorption spectrum and specific rotation of this product with those of the sample previously reported indicates quite definitely that the latter contained among other impurities a considerable amount of cholesterilene.

Like ergosterol [A. Windaus and J. Brunken, *Ann.*, **460**, 227 (1928)] 2,4-cholestadiene in alcoholic solution adds oxygen in the presence of eosin and light to form a stable crystalline peroxide, m. p. 118.5–120.5°, $[\alpha]^{23}\mathrm{D} + 52.8^\circ$ in chloroform.

*Anal.* Calcd. for $C_{27}H_{44}O_2$: C, 80.93; H, 11.08. Found: C, 80.72; H, 11.15.

A further study of these compounds is in progress.

This investigation is being aided by a grant from the International Cancer Research Foundation.

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Received March 21, 1938

# NEW BOOKS

**The Carbon Compounds. A Textbook of Organic Chemistry.** By C. W. Porter, Professor of Chemistry in the University of California. Third revised edition. Ginn and Company, 15 Ashburton Place, Boston, Mass., 1938. viii + 495 pp. 16 × 24 cm. Price, $4.00.

The earlier editions of this well-known book have been reviewed [Whitmore, This Journal, **49**, 1391 (1927); **53**, 3195 (1931)].

"This book constitutes an outline of an elementary course in organic chemistry. Its scope is limited to fundamental principles and general reactions. The publishers have permitted frequent revisions and this policy has made it possible to keep the book in step with recent advances in the field of chemistry."

The present edition includes a new chapter on "Conjugation and Resonance" and a new chapter on "Optical Isomerism."

Henry Gilman

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**La Synthèse Totale en Chimie Organique. Mémoires de MM. Wöhler, Gerhardt, M. Berthelot, Le Bel, Van't Hoff, Jungfleisch, Ladenburg, Pasteur.** (Organic Synthesis from the Elements.) Preface and Commentaries by Marcel Delépine. (Classiques de la Découvert Scientifique.) Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris 6, France, 1937. viii + 145 pp. 13.5 × 19 cm. Price, 21 francs.

The continuity of the present book depends so much upon the Commentaries of Professor Delépine that it seems proper to regard the work as his, a narrative history of the idea and of the fact of the synthesis of organic compounds from the elements, well documented and illustrated with quotations, often very long ones, from the original sources. While the editor-author agrees that many other illustrations might be found for his purpose, the principal points around which he has woven the narrative are as follows: the synthesis of urea by Wöhler and earlier investigations, the discovery of urea by Fourcroy and Vauquelin, the examination of the urine by Rouelle and by Bourdelin, some ideas before Berthelot on the synthesis of organic compounds, Gerhardt's earlier and later opinions, Berthelot's discussion in *La Chimie Organique fondée sur la synthèse*, his synthesis of stearin, of formic acid, of acetylene, of ethylene, of alcohol, and of benzene structure theory (briefly), Van't Hoff on the formulas of structures in space, Le Bel on the relations which exist between the atomic formulas of organic substances and the rotatory powers of their solutions, Jungfleisch's synthesis of *d*- and *l*-tartaric acid from ethylene, Ladenburg's synthesis of coniine, asymmetric decomposition and total asymmetric synthesis. The result is an interesting and coherent account, a cross-section of the history of organic chemistry, which is all the more valuable because no adequate history of organic chemistry as a whole exists at present. The book is illustrated with portraits of Wöhler, Berthelot, Van't Hoff, Le Bel, Jungfleisch, Ladenburg, and Pasteur.

Tenney L. Davis

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**Katalytische Umsetzungen in homogenen und enzymatischen Systemen.** (Catalytic Reactions in Homogeneous and Enzymatic Systems.) By W. Frankenburger, Ludwigshafen/Rhein. Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany, 1937. xi + 444 pp. 22 figs. 15.5 × 24 cm. Price, RM. 34.80; bound, RM. 36.

This book, by one who contributed much to the modern ideas on catalysis, is a comprehensive survey of homogeneously and microheterogeneously catalyzed reactions. It is somewhat disappointing that Dr. Frankenburger, who is an expert on heterogeneous catalysis, has not included heterogeneous reactions in the present volume; nevertheless the work covers a wide field. After a brief and rather non-mathematical introduction reviewing the general theories of reaction rates in elementary and complex reactions, the author discusses catalysis in gas reactions primarily from the point of view of reaction chain mechanism. Several typical reactions are dealt with in detail and the results of their kinetic analysis are presented clearly and yet not dogmatically. The next, and by far the longest, section deals with homogeneous catalysis in liquid mixtures. It is primarily a discussion of acid–base catalysis and of catalysis in oxidation reactions. One misses in the chapter on acid–base catalysis a unified statement of the general acid–base theory and yet its