

From the 1-, 2- and 3-aminophenanthrenes, we have synthesized 1-chlorophenanthrene (m. p. 120–120.5°), 2-chlorophenanthrene (m. p. 85.5–86°), 3-chlorophenanthrene (m. p. 80.5–81.5°), 1-bromophenanthrene (m. p. 109.5–110°), 2-bromophenanthrene (m. p. 95–96°), 3-bromophenanthrene (m. p. 83–84°), 1-iodophenanthrene (m. p. 112.5–113°), 2-iodophenanthrene (m. p. 116–116.5°) and 3-iodophenanthrene (m. p. 83.5–84°). All but one of these compounds have not been described previously. The bromo and iodophenanthrenes are being tested for their ability to form Grignard reagents, for the latter should prove useful in the synthesis of phenanthrene derivatives. The details of these experiments will be published later.

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#### CONCERNING SCHÖNBERG'S CLAIM TO PRIORITY FOR THE BIRADICAL FORMULA OF RUBENES

Sir:

When, indisputably the first to do so, I assigned the biradical formula to the rubenes. I wrote underneath it the two words, "état intermédiaire," in order that there should be no doubt about its role as intermediary in the closed cycle of reactions: rubene + oxygen  $\rightleftharpoons$  dissociable oxide [*Bull. soc. chim.*, **53**, 838 (1933)]. Moreover, I stated explicitly the structural reasons for the existence of this biradical structure, viz., the presence in the rubene molecule of carbons "*du type des carbones aryl-méthaniques, réputés justement pour l'affaiblissement de leur quatrième valence et les phénomènes de dissociation qui en résultent, comme la scission en radicaux libres, Ar<sub>3</sub> ≡ C -, par exemple*" (*ibid.*, p. 837).

Finally, I insisted strongly on the reversibility of the whole process: rubene  $\rightleftharpoons$  dissociable oxide (*ibid.*, p. 836), to the extent of including the word "reversible" in the title of several publications [for example see *Compt. Rend.*, **191**, 1321 (1930)].

I cannot, therefore, now understand Schönberg's insistence, against any evidence, on the priority as to the reversibility in the first period of the transformation, namely, rubene  $\rightleftharpoons$  biradical form; unless he believes that the process may be reversible in its entirety without being reversible in its parts?

It follows that Schönberg has made no original contribution of any kind to the problem of the rubenes, neither to the idea of reversibility nor to the several theories or constitutions which he has unjustly ascribed to himself [see my claim: *Ber.*, **67**, 1021 (1934)].

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#### THE SYNTHESIS OF THE ALDOBIONIC ACID OF GUM ACACIA

Sir:

In 1929 Heidelberger and Kendall [*J. Biol. Chem.*, **84**, 639 (1929)] described a crystalline aldobionic acid, a galactose-glucuronide, obtained from the hydrolysis of gum acacia. This substance was later shown by Challinor, Haworth and Hirst [*J. Chem. Soc.*, 258 (1931)] to be galactopyranose-6-glucuronopyranoside. The configuration of the biose linkage, however, was not at that time fully established. The chemical synthesis of the heptacetyl methyl ester of the aldobionic acid, glucose-6-β-glucuronide, has recently been described by the writers [*Science*, **83**, 353 (1936)]. The present communication deals with an account of the synthesis of the naturally occurring aldobionic acid derived from gum acacia.

When 1-2,3-4 diacetone galactose is condensed with acetobromo glucuronic acid methyl ester [Goebel and Babers, *J. Biol. Chem.*, **111**, 347 (1935)] in ether solution in the presence of silver oxide, the compound 1-2,3-4 diacetone galactose-6-β-triacetylglucuronide methyl ester is formed in yields of 35%. This substance crystallizes in fine needles, melting at 112.5–114°, and shows the rotation  $[\alpha]^{25}_D -68.0^\circ$  in chloroform ( $C = 1.9\%$ ) (Found: C, 51.85; H, 6.45; OCH<sub>3</sub>, 5.39; COCH<sub>3</sub>, 21.5). Upon deacetylation with barium hydroxide and subsequent removal of the acetone groups by boiling with dilute sulfuric acid, the above compound is converted into the crystalline aldobionic acid. The synthetic acid is identical in properties with the naturally occurring aldobionic acid obtained from gum acacia. The melting point of a mixture of the two substances shows no depression.

For purposes of further identification, the heptacetyl methyl ester of the synthetic aldobionic acid was prepared. The latter substance is identical in crystalline structure, solubility and melt-

ing point with the heptacetyl methyl ester obtained from the naturally occurring aldobionic acid. A mixture of the two substances shows no depression of the melting point. The preparation of the heptacetyl methyl ester is carried out as follows. Esterification of the aldobionic acid with diazomethane yields the crystalline methyl aldobionate which melts at  $119^{\circ}$  with effervescence. In water its specific rotation is  $-2.9^{\circ}$  after six minutes, mutarotating to a final value of  $-9.1^{\circ}$  ( $C = 4.2\%$ ) (Found:  $\text{OCH}_3$ , 8.52). On acetylating the ester with acetic anhydride and pyridine, the  $\beta$ -heptacetyl methyl ester of the aldobionic acid is obtained as a well-defined crystalline substance melting at  $202\text{--}203^{\circ}$ , and shows

the rotation  $[\alpha]^{25}_{\text{D}} -17.5^{\circ}$  in chloroform ( $C = 3.3\%$ ) (Found: C, 48.95; H, 5.77;  $\text{OCH}_3$ , 4.73;  $\text{COCH}_3$ , 44.7).

In view of the fact that  $\alpha$ -acetobromo glucuronic acid methyl ester, when condensed with alcohols in the presence of silver oxide, has been found to yield only  $\beta$ -glucuronides, the biose linkage of the gum acacia aldobionic acid must possess the  $\beta$  configuration. The acid can be definitely assigned, therefore, the structure of a galactopyranose-6- $\beta$ -glucuronopyranoside.

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## NEW BOOKS

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**The Chemistry of Natural Products Related to Phenanthrene.** By L. F. FIESER, Associate Professor of Chemistry, Harvard University. American Chemical Society Monograph. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y., 1936. xii + 358 pp.  $15.5 \times 23.5$  cm. Price, \$6.50.

During the past five or six years an amazing increase in research activity in the phenanthrene field has taken place. This has been due especially to the recognition that many naturally occurring, often biologically important, classes of organic compounds are derivatives of phenanthrene or one of its hydrogenation products. Thus, characterized as hydrophenanthrene derivatives are the alkaloids of the morphine and aporphine groups, the acids from resins of conifers and the triterpenoid saponins. Included also are the animal and plant sterols and the many products of related structure probably formed by biological oxidation or reduction of sterols, namely, the bile acids, the male and female sex hormones, the cardiac glycosides or heart poisons secreted by toads and antirachitic agents. Likewise, the cancer-producing hydrocarbons nearly all contain the phenanthrene nucleus. This volume comprises a comprehensive résumé of these fields.

The author has introduced his subject with a general discussion of the chemistry of phenanthrene in order to provide a background for the consideration of derivatives which are of interest either as degradation products or as intermediate products in the synthesis of the compounds under consideration. Each of the succeeding chapters is devoted to the chemistry of an individual group of closely related phenanthrene compounds.

The attempt in this book to present a well-rounded summary of the more significant and useful observations in each of the separate fields and to give prominence to corre-

lating principles and to other matters of central interest has been completely successful. The material has been selected with great care, skillfully organized and written in such a clear, concise way as almost to leave the reader with the impression that these complicated subjects in organic chemistry are actually relatively simple.

The active interest in phenanthrene compounds is at its peak and the publication of this book could not have been more timely. It will serve the general organic chemist as an excellent review of a major field of study, and will prove invaluable to the investigator along these lines as a survey of the significant contributions published prior to February, 1936.

The book is so well printed and so free from errors, and the subject is so superbly presented that the reviewer can merely give it unreserved commendation. No recent book in any specialized field of organic chemistry will prove as generally attractive and useful as this one.

ROGER ADAMS

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**Lehrbuch der organischen Chemie.** (Textbook of Organic Chemistry.) By A. F. HOLLEMAN. Twentieth revised and enlarged edition by Friedrich Richter. Walter de Gruyter and Company, Genthiner Strasse 38, Berlin W 10, Germany, 1935. xii + 546 pp. 78 figs.  $15 \times 23$  cm. Price, bound, RM. 14.

The latest Holleman Lehrbuch, rewritten by Friedrich Richter, is undoubtedly one of the best texts of organic chemistry. The science is considered from the experimental viewpoint of structural evidence, in a manner which should encourage the student to correlate his knowledge and think in chemical terms, rather than memorize facts. By tabulating physical data and condensing purely descrip-