parent hydrocarbon, cholanthrene, by three different methods.

THE CANCER HOSPITAL (FREE) J. W. COOK
LONDON, ENGLAND G. A. D. HASLEWOOD
RECEIVED JUNE 11, 1935

METHYLCHOLANTHRENE

Sir:

In reply to the communication of J. W. Cook and G. A. D. Haslewood under the above title, I should like to disclaim any intention on the part of Newman and myself of underestimating the work of the English investigators on methylcholanthrene. Our note [THIS JOURNAL, **57**, 961 (1935)] was the third of a series of papers on the subject, and in the first paper [Fieser and Seligman, *ibid.*, **57**, 228 (1935)] reference was made to Cook and Haslewood's proof of the structure of methylcholanthrene and to their demonstration, with Kennaway, of its carcinogenic activity. Further reference to the history of the problem seemed beyond the scope of our brief note.

It is quite true that our statement regarding the yield was misleading, and I should like to present an explanation which was omitted before merely in the interest of brevity. Our purpose in estimating the approximate yield of methylcholanthrene from desoxycholic acid by the method first described by Wieland and Dane was to show that the new preparation from cholic acid (which is considerably shorter and more economical) yields about the same amount of material. In the absence of any statements in the literature regarding the yields of recrystallized acids in the first two steps, we used the best results of experiments of our own, namely, 60% for the oxidation and 80% for the reduction. For the cyclization, we took Cook and Haslewood's figure of 30% as being more accurate than the yield (39%) reported by Wieland and Schlichting [*Z. physiol. Chem.*, **150**, 267 (1925)] for a small-scale experiment. For the final step we used the yield of 30% obtained by Cook and Haslewood. I believed that our estimate of 4.3% was a fair one, and the fact that the matter of yields has not been emphasized by the other investigators may excuse us for having considered the details of the calculation sufficiently unimportant to be covered by the word "approximately."

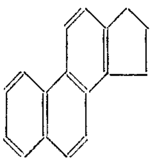
I appreciate the courtesy of Cook and Haslewood in welcoming our participation in the work of developing the important field opened up by the fundamental discoveries of these investigators and their associates at the Cancer Hospital, and I am glad to acknowledge our indebtedness to the English group in providing the inspiration for our efforts to contribute to the cancer problem.

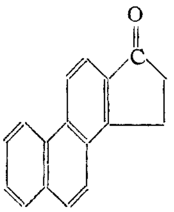
CONVERSE MEMORIAL LABORATORY LOUIS F. FIESER
HARVARD UNIVERSITY
CAMBRIDGE, MASS.
RECEIVED JUNE 18, 1935

THE SYNTHESIS OF 1,2-CYCLOPENTENOPHENANTHRENE AND RELATED COMPOUNDS

Sir:

β-(2-Phenanthryl)-propionic acid (m. p. 177–177.5°) was obtained through the malonic ester reaction from 2-phenanthrylmethyl bromide; cyclization of the acid chloride by stannic chloride gave 1'-keto-1,2-cyclopentenophenanthrene (m. p. 183–184°); by Clemmensen reduction the ketone was converted to 1,2-cyclopentenophenanthrene (I), which was identical with the product prepared by Cook's method [*J. Chem. Soc.*, 1098 (1933)]. β-(3-Phenanthryl)-propionic acid (m. p. 156–157°) was prepared in a similar manner; the product of cyclization (m. p. 140–140.5°) is probably 1'-keto-2,3-cyclopentenophenanthrene, although the 3,4-structure is not excluded.


(I)

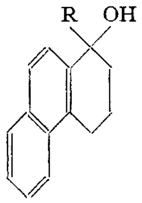


(II)

Of considerable interest as a basic structure of a number of important natural products as the sex hormones is the ketone, 3'-keto-1,2-cyclopentenophenanthrene (II). In order to obtain this ketone we have synthesized β-(1-phenanthryl)-propionic acid through the following series of reactions: phenanthrene ⟶ 1-benzoylphenanthrene ⟶ 1-phenanthraldehyde ⟶ 1-phenanthrylcarbinol ⟶ 1-phenanthrylmethyl bromide ⟶ β-(1-phenanthryl)-propionic acid. The preparation of 1-benzoylphenanthrene has already been described [Bachmann, THIS JOURNAL, **57**, 555 (1935)]. The oxime (m. p. 186°) of this ketone was found to undergo a Beckmann rearrangement to 1-phenanthroic acid anilide (m. p. 245°); from 70 g. of 1-benzoylphenanthrene we obtained

67 g. of the anilide. Reaction of the acid anilide with phosphorus pentachloride followed by reduction of the product by stannous chloride and hydrogen chloride in absolute ether yielded the new phenanthrene aldehyde 1-phenanthraldehyde (m. p. 110–111°; yield, 65%). These reactions now make it possible to prepare many 1-substituted phenanthrene derivatives hitherto difficult to obtain, and we are engaged in the preparation of such compounds. Reduction of the aldehyde to the carbinol (m. p. 165°), followed by a malonic ester condensation with the carbinol bromide (m. p. 97°) gave β-(1-phenanthryl)-propionic acid (m. p. 189–189.5°); experiments on the cyclization of this acid are not yet complete.

The excellent researches of Cook and coworkers [Cook, Dodds, Hewett and Lawson, *Proc. Roy. Soc.* (London), **114,** 278 (1934)] have shown that oestrogenic property is possessed by a variety of polycyclic compounds; and we are having the keto-cyclopentenophenanthrenes and derivatives tested for this property. We have also prepared three 1-hydroxy-1-alkyl-1,2,3,4-tetrahydrophenanthrenes (III) in crystalline state in which the alkyl group R is methyl (m. p. 86–86.5°), ethyl (m. p. 57–57.5°) and *n*-propyl (m. p. 86–87°); these compounds likewise are being tested for oestrogenic activity.



(III)

The physiological tests are being made by Dr. James Bradbury at the University of Michigan Hospital. The details of the experiments will be published later.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
W. E. BACHMANN

RECEIVED JUNE 13, 1935

THE PREPARATION OF MONOCHLOROACETOCATECHOL

Sir:

In the synthesis of adrenaline according to the method of Stolz [*Ber.*, **37,** 4149 (1904)] the preparation of monochloroacetocatechol is necessary. Chloroacetic acid, catechol and phosphorus oxychloride are mixed together and refluxed on the steam-bath. At the end of an hour the material in the flask is recrystallized from hot water. Using this method as it stands, repeated preparation shows large amounts of tars which obliterate much of the yield. Oxidation of the catechol must also be repressed for greater yields. To carry out this purpose the following method was used.

Fifty grams each of monochloroacetic acid, catechol, and *freshly distilled* phosphorus oxychloride were mixed together in a one-liter short-necked flask fitted with reflux condenser and a tube through which sulfur dioxide was passed. A tube was attached to the end of the reflux condenser to lead away hydrogen chloride gas evolved in the reaction, and the sulfur dioxide. After the flask was filled with the sulfur dioxide from a tank, heating was started, a steady stream of gas always flowing. At the end of an hour heating was stopped, the purple crystals of crude chloroacetocatechol crystallized from hot water, decolorized with acid, Norite and sodium sulfite, and again crystallized. The light violet tinged crystals were washed with absolute alcohol, and finally ether. The yield was 53.6 g., m. p. 173°. Without these modifications, namely, the sulfur dioxide atmosphere and freshly distilled phosphorus oxychloride, the yield was 8.3 g.

COLUMBIA UNIVERSITY
NEW YORK CITY
HENRY D. HOBERMAN

RECEIVED JUNE 15, 1935

THE RAMAN SPECTRUM OF RUBBER

Sir:

It has been previously reported that the Raman effect is exhibited by rubber as a continuous scattering together with the presence of broad bands [Franklin and Laird, *Phys. Rev.*, **36,** 147 (1930); Busse, *J. Phys. Chem.*, **36,** 2862 (1932)]. Busse attributed this result to the viscosity of the solutions or to the possibility that the rubber groups respond to a wide range of frequencies. However, viscous solutions of polysterol in carbon tetrachloride give a line spectrum [Signer and Weiler, *Helv. Chim. Acta,* **15,** 649 (1932)]. As to the second explanation, this does not seem to be the nature of the Raman effect [Bär, *Helv. Phys. Acta,* **4,** 369 (1931); Bär, *Z. Physik,* **79,** 455 (1932)]. The Raman effect has been investigated extensively for terpenes other than rubber.

The bands and continuous background for rubber appear to be due to fluorescence of im-