

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.

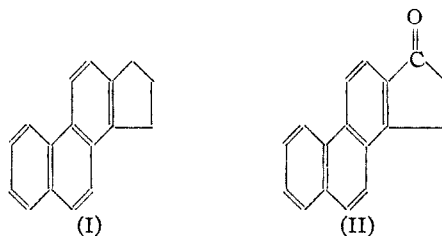
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RECEIVED JUNE 18, 1935

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.



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 \longrightarrow 1-benzoylphenanthrene \longrightarrow 1-phenanthraldehyde \longrightarrow 1-phenanthrylcarbinol \longrightarrow 1-phenanthrylmethyl bromide \longrightarrow 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