TABLE I

Salt	Density at 25°
$LaCl_3$	0.99707 + 0.00912 *P*
$CeCl_3$	.99707 + .00915 *P*
$PrCl_3$	.99707 + .00917 *P*
$NdCl_3$	.99707 + .00920 *P*

where *P* is the weight percentage of the salt. These formulas reproduce the experimental data within the above stated accuracy except for the most concentrated solution of lanthanum chloride (4.67%) whose observed density was 1.0403 instead of the 1.0396 calculated.

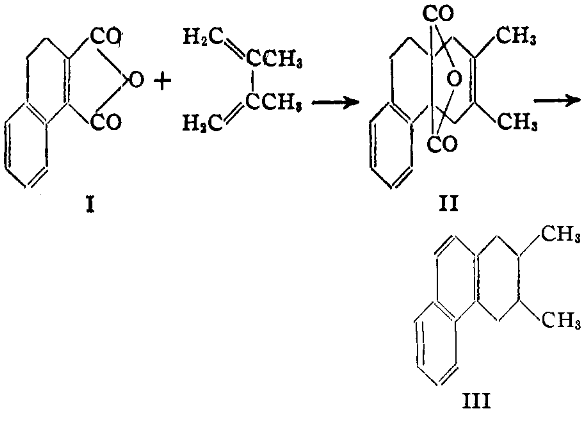
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, N. H.
RECEIVED JUNE 11, 1935

COMMUNICATIONS TO THE EDITOR

A NEW PHENANTHRENE SYNTHESIS

Sir:

A new route to polynuclear aromatic and hydroaromatic types containing the phenanthrene ring system has been found in the addition of dienes to cyclic maleic anhydride derivatives such as 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (I) [von Auwers and Möller, *J. prakt. Chem.*, **217,** 124 (1925)]. The adduct II, m. p. 75.5–76.5° (calcd.: C, 76.57; H, 6.45. Found: C, 76.56; H, 6.44) was obtained from I and 2,3-dimethylbutadiene in 97% yield.



I

II

III

(All melting points reported are corrected.) Hydrogenation, using Adams' catalyst, gave the dihydro adduct, m. p. 117–118°. On fusing II with potassium hydroxide at 320–400° and distilling the product, there was obtained in 70% yield a hydrocarbon (b. p. 194–197° (19 mm.)) having the analysis and properties (resistant to catalytic hydrogenation) corresponding to the formula III. Hydrogen was evolved during the fusion. Dehydrogenation of III with selenium gave in excellent over-all yield a hydrocarbon which we believe to be pure 2,3-dimethylphenanthrene, m. p. 78–78.5° (calcd.: C, 93.16; H, 6.85. Found: C, 92.86; H, 7.08); picrate, m. p. 146–147°; quinone, m. p. 237.5–238.5° (calcd.: C, 81.32; H, 5.13. Found: C, 81.23; H, 5.37); quinoxaline, m. p. 208–209°. The constants found for the last two derivatives agree well with the values reported by Haworth, Mavin and Sheldrick [*J. Chem. Soc.*, 454 (1934)], but our hydrocarbon melts considerably higher than that synthesized by these investigators. The structure of our material was established by oxidation with nitric acid to pyromellitic anhydride.

In a similar reaction series, using butadiene, we obtained phenanthrene, m. p. 96.5–97.5°, showing no depression when mixed with a purified sample from coal tar (m. p. 97–98°).

Starting with ethyl γ-[1-naphthyl]-butyrate and oxalic ester, we have synthesized 3,4-dihydrophenanthrene-1,2-dicarboxylic acid anhydride, m. p. 263.5–264.5° (calcd.: C, 76.77; H, 4.04. Found: C, 76.83; H, 4.37), and from it the 2,3-dimethylbutadiene adduct, m. p. 196–196.5°. Dehydrogenation of the dihydrophenanthrene derivative with sulfur gave in good yield phenanthrene-1,2-dicarboxylic acid anhydride, m. p. 311–312° (calcd.: C, 77.39; H, 3.25. Found: C, 77.55; H, 3.62). By the same method naphthalene dicarboxylic acid anhydride was obtained from I in 76% yield.

In view of the active interest in the types of compounds made available by these new synthetical methods, and considering the recently reported attempts to apply to the problem other modifications of the Diels–Alder reaction [Cohen, *J. Chem. Soc.*, 429 (1935); Lehmann and Paasche, *Ber.*, **68,** 1147 (1935)], we wish to reserve for full description and further study the methods and compound types indicated above.

CONVERSE MEMORIAL LABORATORY L. F. FIESER
HARVARD UNIVERSITY E. B. HERSHBERG
CAMBRIDGE, MASSACHUSETTS

RECEIVED JULY 22, 1935

NEW MEASUREMENTS OF PREVIOUSLY UNKNOWN LARGE INTERPLANAR SPACINGS IN NATURAL MATERIALS

Sir:

There is at present intense interest and importance in the discovery and measurement of very large interplanar spacings (for example, greater than 40 Å.) in natural materials such as proteins, rubber, cellulose, etc. By ordinary x-ray diffraction technique interferences corresponding to such spacings are not resolved from the blackening of the photographic film due to the undeflected primary x-ray beam. Recourse must be taken, therefore, to the following procedures: (1) with a given primary x-ray wave length, usually the Kα of copper, decrease pinhole sizes to 0.005 inch, increase specimen to film distances from 5 cm. usually employed to 20–30 cm., and center very small lead beads with extraordinary care over the point of impingence on the film of the unabsorbed primary beam; (2) increase the x-ray wave length λ by the use of magnesium or aluminum targets, since sin θ (2θ = diffraction angle) increases with the value of λ for a given spacing. We have succeeded in improving the technique of both methods (for the latter by placing the vacuum camera in a magnetic field to deflect scattered electrons which fog diffraction films) to such an extent that definite and reproducible results on unsuspected large spacings have been obtained for a variety of materials:

(1) Living nerve: various orders of a spacing of 171 Å. in fresh medullated nerve, due probably to oriented fluid crystals of the myelin sheath. This *c* spacing lies radial and perpendicular to the long direction of the axon [for extended accounts see *Science*, **80,** 567 (1934); **82,** 44 (1935); *Radiology*, in press.]

(2) Collagen and gelatin: in collagen (catgut) beautifully resolved meridianal interferences (along fiber axis) in 4 orders of a spacing of 220 or 440 Å. (204 or 408 for chromicized catgut), and an equatorial or lateral spacing of 48 Å. which is exceptionally sensitive to any treatment, even sterilization. These large spacings *are completely absent* in gelatin, whereas the outer ordinary patterns for collagen and stretched gelatin are identical.

(3) Keratin: a lateral or equatorial spacing of 81 Å., verifying a prediction by Astbury that a lateral spacing of approximately 90 Å. should exist.

(4) Gel rubber: for the fraction of rubber insoluble in ether a well defined ring for 58 Å. in unstretched rubber, which segments into equatorial sickles on stretching. Sol rubber gives *no* such large spacing interferences.

(5) Cellulose: for cellulose there is definite but somewhat diffuse scattering at very small angles. Equatorial maxima like small arrow heads, but thus far unresolved into a series of individual spots, run out from this halo.

DEPARTMENT OF CHEMISTRY G. L. CLARK
UNIVERSITY OF ILLINOIS E. A. PARKER
URBANA, ILLINOIS J. A. SCHAAD
W. J. WARREN

RECEIVED JULY 12, 1935

4′-HYDROXY-1,2-BENZPYRENE

Sir:

In view of the statement of Winterstein, Vetter and Schön [*Ber.*, **68,** 1079 (1935)] that they are attempting to prepare the hitherto unknown 4′-hydroxyl derivative of 1,2-benzpyrene [numbering system of Cook and Hewett, *J. Chem. Soc.*, 398 (1933)] by the dehydrogenation of 4′-hydroxy-1′,2′,3′,4′ - tetrahydro - 1,2 - benzpyrene, we may report the preparation of the compound in question by another method. In previous studies of the action of selenium on 4′-keto-1′,2′,3′,4′ - tetrahydro - 1,2 - benzpyrene [Cook and Hewett, *loc. cit.;* Winterstein and Vetter, *Z. physiol. Chem.*, **230,** 169 (1934)] the only pure product isolated was 1,2-benzpyrene. Using the amount of selenium required for the removal of two hydrogen atoms and heating for two hours at 310–320°, we have isolated 4′-hydroxy-1,2-benzpyrene in small amounts. Using sulfur in place of selenium (seventy-five minutes at 220–230°) we obtained the completely pure hydroxy compound in 19% yield from the crude ketone.

4′-Hydroxy-1,2-benzpyrene forms yellow elongated plates, m. p. 218–219°, corr., from benzene–ligroin (calcd.: C, 89.52; H, 4.51. Found: C, 89.59; H, 4.76). The corrected melting points