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.

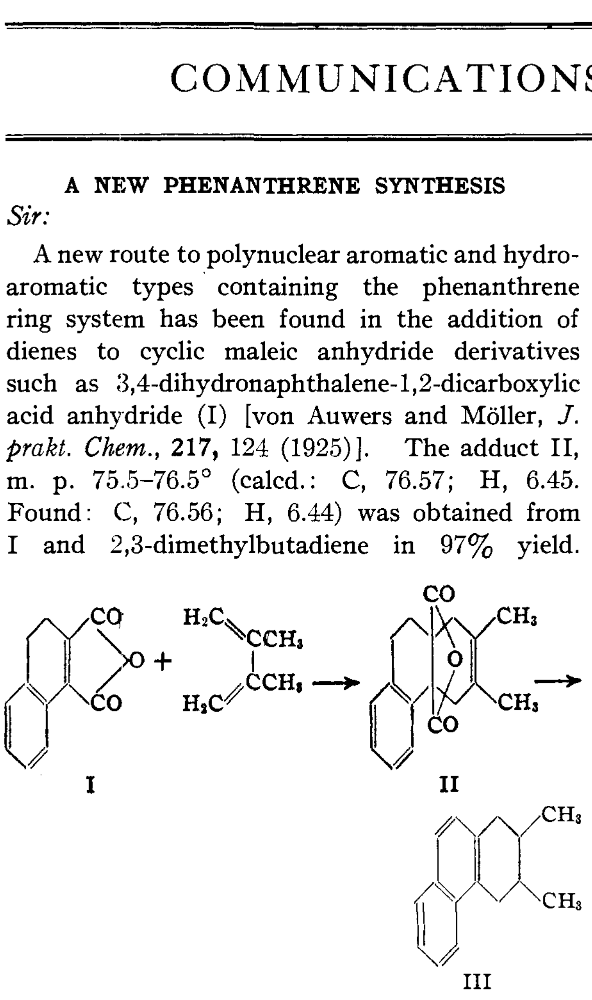
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, N. H.
RECEIVED JUNE 11, 1935

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.



(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 of a few derivatives are as follows: acetate, 194–195°; benzoate, 191–192°; methyl ether, 183–184; carboxymethyl derivative, 239–240°. It is characteristic of the hydroxy compound and of the above derivatives that the red solution in concentrated sulfuric acid acquires, on the addition of a drop of concentrated nitric acid, a transient green color changing to deep blue.

The preparation of these and other derivatives desired for biological experimentation will be described later.

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

RECEIVED JULY 22, 1935

THE PEROXIDE EFFECT IN THE CANNIZZARO REACTION

Sir:

The theory of Haber and Willstätter [*Ber.*, **64**, 2844 (1931)] that the Cannizzaro reaction has a chain mechanism, catalyzed by heavy metal ions, such as ferric ion, has been investigated in this Laboratory. Catalysis by ferric ion was indeed found to take place under ordinary conditions. However, when special precautions were taken to use peroxide-free aldehydes, and to run the reaction in the absence of oxygen, no Cannizzaro reaction took place, nor did the addition of ferric iron cause any appreciable degree of reaction. Thus it would appear that the Cannizzaro reaction is catalyzed primarily by peroxides, rather than by the heavy metals, and that the function of the latter is to facilitate the formation of peroxides in the mixture, being without any direct effect on the Cannizzaro reaction itself.

This has been shown to be the case with benzaldehyde, tolualdehyde and anisaldehyde. Typical results in the case of tolualdehyde and 55% potassium hydroxide solution are as follows.

CANNIZZARO REACTION WITH TOLUALDEHYDE

Technique of addition	Peroxide content of aldehyde	Time, hrs.	Added reagents	Extent Cannizzaro, %
Air	3+	8	......	33
Vac	Neg.	8	......	0
Air	3+	22	......	91
Vac	Neg.	22	......	2
Vac	Neg.	22	0.1 g. $FeCl_3$	12
Air	4+	20	......	100
Vac	Neg.	20	.2 g. $FeCl_3$	8
Vac	Neg.	20	.5 g. toluic acid	0
Oxygen	Neg.	20	.2 g. $FeCl_3$ and solution saturated with oxygen	38

Further experiments along these lines are in progress in this Laboratory, and a comprehensive report of the research will soon be published.

GEORGE HERBERT JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO M. S. KHARASCH
CHICAGO, ILLINOIS (MRS.) MABEL FOY

RECEIVED JULY 13, 1935

A MICRO QUINHYDRONE–SILVER CHLORIDE CELL FOR PRECISION E. M. F. STUDIES ON HEAVY WATER

Sir:

For the purpose of studying the exchange reaction

$$QH_2 \text{ (deuteroquinone)} + 2HCl = QH_2 \text{ (hydroquinone)} + 2DCl$$

we have investigated the reliability of the silver chloride electrode using a micro technique, applicable to heavy water, where the quantities of solution available for rinsing are severely limited.

The cells, which were of 2–4 cc. capacity, were similar in construction to the macro type employed by Harned and Wright [THIS JOURNAL, **55**, 4851 (1933)]. The Type A did not permit rinsing the silver chloride electrode compartment, nor did it have a long capillary tube to minimize diffusion of quinhydrone to the silver chloride electrode. In type B, these factors and in addition space for duplicate electrodes of each kind were provided. Oxygen was removed from the final solutions by repeated evacuation, followed by backing with nitrogen before admitting the solutions to the cells. Eastman quinhydrone was recrystallized at *p*H 5 to 6 in an atmosphere of nitrogen until it melted sharply between 170.5–171.0° (corr.).

The limiting factor appears to be the accuracy with which the concentration of the acid (0.01 *M*) can be prepared using small quantities. Constant boiling (H_2O) acid was added from a 1-cc. micro weight buret to 15 to 25 cc. of D_2O–H_2O mixtures of known density, using a balance accurate to 0.02 mg. We obtained more reproducible results in the quinhydrone half cell with spiral platinum wires than with large foils. The preparation of the silver chloride electrodes is described elsewhere [Armbruster and Crenshaw, THIS JOURNAL, **56**, 2525 (1934)]. They were washed well in distilled water, and then repeatedly with small amounts of the cell solution. In the micro cells, an equilibrium value is obtained within one-half hour, and is maintained to within 0.05 mv. for two to four hours, followed by a slow drift. The micro results are as reproducible as with the macro technique, the average value being only 0.01 mv. less than that computed from the Harned and Wright empirical eq. (2); namely, for $m = 0.01$; $E = 0.23549$ v.

Type	HCl, M	$E_{0.01}$, mv.
A	0.01002	0.23552 ± 0.07
	.01002	.23545 ± .04
	.01008	.23544 ± .03
B	.01006	.23550 ± .06
	.01006	.23548 ± .03

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY

VICTOR K. LA MER
MARION H. ARMBRUSTER

RECEIVED MAY 23, 1935

THE E. M. F. OF THE QUINHYDRONE ELECTRODE IN HEAVY WATER. THE ACIDIC DISSOCIATION OF DEUTEROQUINONE

Sir:

By measuring the e. m. f. of the cell

Ag, AgCl, HCl (0.01 M), Quinhydrone ($Q \cdot QH_2$), Pt (I)

corresponding to the processes

$$2HCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QH_2;\ E_H \quad (1)$$
$$2DCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QD_2;\ E_D \quad (2)$$

when carried out in ordinary and heavy water, we obtain the free energy of the exchange process

$$2DCl(0.01\ M) + QH_2 = 2HCl(0.01\ M) + QD_2;\ E_D - E_H \quad (3)$$

If we assume that the activity of the chloride ion is the same in both waters, equation (3) may be considered as the difference of the dibasic acid dissociations

$$QH_2 = Q^{=} + 2H^+ \text{ (in } H_2O);\ K_H \quad (4)$$
$$QD_2 = Q^{=} + 2D^+ \text{ (in } D_2O);\ K_D \quad (5)$$

where K_H, the average dissociation constant, equals $K_1K_2 = (1.75 \times 10^{-10})(4 \times 10^{-12}) = 2.64 \times 10^{-11}$ for ordinary water [S. E. Sheppard, *Tr. Am. Electrochem. Soc.*, Preprint 39 (1921); La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923)].

Extrapolation to pure D_2O indicates that $E_D - E_H = 0.0345$ v. Hence $\log K_H/K_D = 0.0345/0.05911 = 0.5837$, or $K_H/K_D = 3.84$, a result which accords with the decrease in acidic dissociation of other weak acids in D_2O; *e. g.*, deutacetic acid [Lewis and Schutz, THIS JOURNAL, **56**, 1002 (1934)], chloroacetic acid [*ibid.*, **56**, 1913 (1934)].

N_{D_2O}	Molality HCl	$E_{0.0\ m}$ mole/1000 g.	$E_{0.01m}$ mole/55.5 moles
0	0.011182	0.23548	0.23548
	.010855	.23541	.23541
0.103	.01192	.23736	.23677
.3454	.013576	.24604	.24409
	.00880	.24614	.24419
.5109	.01127	.25301	.25016
	.01018	.25306	.25021
.6925	.008844	.26173	.25770
	.009718	.26169	.25766
.9240	.010446	.27190	.26685
	.009991	.27195	.26690
(1.0000)		(.2752)	(.2700)

The measurements were made at 25° with Type B micro cells as described [La Mer and Armbruster, THIS JOURNAL, **57**, 1510 (1935)] where the reliability of the micro technique is established. In the last column of the table the e. m. f. is corrected to exactly 0.01 mole HCl/55.5 moles solvent for purposes of comparison. The normal potential is 0.4774 volt, but in heavy water the value extrapolated linearly would be 0.5119 v. if we make the highly plausible assumption that the activity coefficients in D_2O and H_2O are identical. N_{D_2O}, the mole fraction of heavy water was computed from density measurements using the formula of La Mer and Baker [*ibid.*, **56**, 2641 (1934)]. Both curves deviate from linearity at low D_2O concentrations. Experiments are in progress to check the reliability of extrapolation. The investigation is being continued, using the deuterium gas electrode to study the reaction, $QD_2 + H_2 = QH_2 + D_2$.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY

VICTOR K. LA MER
SAMUEL KORMAN

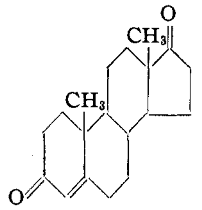
RECEIVED JULY 22, 1935

THE OXIDATION AND REDUCTION OF DEHYDROANDROSTERONE

Sir:

It has been shown by Gallagher and Koch [*J. Biol. Chem.*, **104**, 611 (1934)] that highly active testicular extracts are sensitive to hydrogen-ion concentration, and show a decided decrease in their activity when boiled with alkalies, whereas active extracts obtained from male urine do not show this behavior. This fact strongly indicates that the active compound present in the testes is different in structure from that of androsterone. It is also known that this instability toward alkalies is a characteristic property of the corpus luteum hormone.

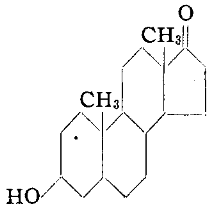
This similarity in behavior suggests that the testicular hormone may possess in a portion of its molecule a structure closely related to that which is present in the corpus luteum hormone. Therefore it seemed important to us to prepare a compound structurally related to both the corpus luteum hormone and to androsterone. Such a substance would be the unsaturated diketone, Δ^4-etio-cholen-dione-3,17. (I)



I

This compound has now been prepared in this Laboratory by oxidation of the dibromide of dehydroandrosterone (the dehydroandrosterone used in these experiments was prepared by Francis B. Cramer according to our method [Wallis and Fernholz, THIS JOURNAL, **57**, 1379 (1935)] with chromic acid by a method similar to that used in the preparation of the corpus luteum hormone [Fernholz, *Ber.*, **67**, 1855, 2027 (1934)]. It melts at 170° (uncorr.), $[\alpha]^{30}\mathrm{D}$ $+199°$ in chloroform. Physiological investigations are being made to determine whether it possesses properties similar to the active principle occurring in testicular extracts.

We have also carried out experiments on the hydrogenation of dehydroandrosterone, and have found that in alcoholic solution, under proper conditions, 3-hydroxy-etioallocholanone-17 (II)



II

is easily obtained by hydrogenation with palladium black. This product melts at 172° (uncorr.), $[\alpha]^{26}\mathrm{D}$ $+88.6°$ in methyl alcohol. A mixed melting point with an authentic specimen of the hydroxy ketone showed no depression. In acetic acid solution both the double bond and the ketone group in dehydroandrosterone are hydrogenated. This also occurs when platinum black is used as the catalyst.

The experimental details of the preparation of these compounds together with the results of the physiological tests will be reported at a later date.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.
EVERETT S. WALLIS
E. FERNHOLZ

RECEIVED JULY 15, 1935

NEW BOOKS

Dictionnaire de la Chimie et de ses Applications. (Dictionary of Chemistry and its Applications.) By CLÉMENT DUVAL, Docteur ès Sciences physiques, RAYMONDE DUVAL, Docteur ès Sciences physiques, and ROGER DOLIQUE, Dr. ès Sciences phys. Pharmacien. Preface by H. Luc, Directeur général de l'Enseignement technique. Hermann & Cie., 6 Rue de la Sorbonne, Paris, France, 1935. xxxii + 747 pages. 13.5 × 19 cm., paper covers, price, 90 francs.

This excellent little dictionary provides the reader of French scientific literature with brief guiding definitions of about 20,000 terms in chemistry and related fields, including a number of French trade names not easily found elsewhere. Named types of apparatus are defined by use only and are not described. The list of names of minerals appears to be especially complete.

The modernity of the work is indicated by the inclusion of deuterium but not tritium. No etymological information is given nor is the correct syllabification or pronunciation indicated. It is obviously a book to be consulted by the reader who wishes to acquaint himself with the meaning of an unfamiliar term and for this reason alone deserves a place on the shelf of a reference library.

WILLIS A. BOUGHTON

The Application of Absorption Spectra to the Study of Vitamins and Hormones. By R. A. MORTON, D.Sc., Ph.D., F.I.C., The University of Liverpool. Published by Adam Hilger, Ltd., 98 Kings Road, Camden Road, London, N. W. 1, England, 1935. 73 pp. 25 figs. 16 × 25.5 cm. Price, per copy including postage, 10s./4d.

This little book consists of eight essays, seven dealing with specific vitamins, and one with a few hormones. It seems to furnish the text for an unwritten sermon extolling the possibilities of the spectroscopic method in organic