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
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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.

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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.

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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