NOTES.

Identification of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydrophenanthrene.* By FELIX BERGMANN and ERNST BERGMANN.

THE liquid hydrocarbon recently obtained in thermolysis and dehydrogenation experiments from cholesteryl chloride (this vol., p. 1019) and assumed to be 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene on the basis of its physical constants has now been identified by converting it and an authentic sample of the octahydrophenanthrene into the same crystalline derivative.

9-*Acetyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrophenanthrene.*—To a solution of authentic octahydrophenanthrene (4·65 g.) and acetyl chloride (2·5 c.c.) in nitrobenzene (25 c.c.), aluminium chloride (7·5 g.) was added at 0°; the red mass was kept at 5° for 24 hours, decomposed with ice and concentrated hydrochloric acid, and treated with steam. The material extracted from the residue with chloroform was distilled in a vacuum (0·15 mm.); the product distilling between 147° and 150° crystallised spontaneously. The *ketone* separated from methyl alcohol at −70° in plates, m. p. 52—53°; yield, 2 g. (Found: C, 84·8; H, 8·8. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%).

Semicarbazone. The ketone (1 g.), semicarbazide hydrochloride (1·1 g.), and sodium acetate trihydrate (1·4 g.) were boiled for 3 hours in aqueous methyl alcohol. The *semicarbazone*, obtained by addition of water, was crystallised successively from methyl alcohol, butanol, and xylene–ligroin; m. p. 201—203° (Found: C, 71·7; H, 7·7; N, 15·2. $C_{17}H_{23}ON_3$ requires C, 71·6; H, 8·0; N, 14·7%).

The degradation product (1·5 g.) from cholesteryl chloride was treated in the same way. The crude acetyl derivative was converted into the semicarbazone, which after the described purification was identified with the above product by the method of mixed m. p.

We are indebted to Prof. E. Mosettig (Virginia University) for a gift of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, June 19th,* 1939.]

Studies of the ortho-*Effect. Part V. The Alkaline Hydrolysis of Ethyl Anthranilate.* By J. J. GORDON and H. B. WATSON.

KINETIC studies of the alkaline hydrolysis of substituted ethyl benzoates (Ingold and Nathan, J., 1936, 222; Evans, Gordon, and Watson, J., 1937, 1430) have shown that groups in the *m*- or *p*-position influence the energy of activation to a marked degree but leave the *P* factor of the equation $k = PZe^{-E/RT}$ almost unchanged. On the other hand CH_3, Cl, and NO_2 in the *o*-position cause an appreciable decrease in the value of *P*, and it has been suggested (J., 1937, 1421) that interaction occurs, in the transition complex, between the *o*-substituent and the

doubly linked oxygen of the ester grouping. This view is made probable by the fact that *o*-fluorine (which cannot so interact) causes no decrease in *P*.

The postulate of a similar interaction in the anion of an *o*-substituted benzoic acid appears to be unnecessary, in several cases at least, since Jenkins (this vol., p. 640) finds that the relatively high dissociation constants of the *o*-halogeno- and *o*-nitro-acids find a complete interpretation on the basis of inductive effects alone. *o*-Methoxyl probably comes into the same category, but the newer view is not applicable to salicylic and *o*-toluic acids. The low *P* values found in the hydrolysis experiments, also, are still explained most easily by the hypothesis of group interaction, which is also applicable to related observations of esterification and acid hydrolysis (see *Ann. Reports*, **1938**, **35**, 246).

We have now made a kinetic study of the alkaline hydrolysis of both ethyl *m*-aminobenzoate (b. p. 144°/5 mm.) and ethyl anthranilate (prepared by the Fischer–Speier method, b. p. 105°/5 mm.). The medium was 85% alcohol, and the method of experiment identical with that described by Evans, Gordon, and Watson (*loc. cit.*). Our results are recorded below, together with those for ethyl benzoate for purposes of comparison.

R in $C_6H_4R{\cdot}CO_2Et$.	$10^3k_{50°}$.	$10^3k_{35°}$.	$10^3k_{25°}$.	E(cals.).	10^2P.
m-NH_2	3·21	0·830	0·308	18,100	2·15
o-NH_2	0·647	0·146	0·0476	20,000	8·32
H	6·28	1·68	0·621	17,700	2·17

The value of E for the *m*-amino-compound is slightly above that for ethyl benzoate (compare Tommila and Hinshelwood, who used aqueous acetone as medium, J., **1938**, 1801); it appears that the mesomeric effect of the group is to some extent relayed inductively to the *m*-position. *P* is not affected, however. For ethyl anthranilate the value of E is identical with that found by Ingold and Nathan (*loc. cit.*) for its *p*-isomeride, but the *P* factor is somewhat *high* (about 100 times greater than the value for ethyl *o*-nitrobenzoate).

Interaction between the amino-group and the doubly linked oxygen of carbethoxyl (in the transition complex) can hardly be doubted, since Chaplin and Hunter (J., **1938**, 375) find that ethyl *o*-acetamidobenzoate is chelated under normal conditions. Ethyl anthranilate is the first ester to be studied in which the group in the *o*-position has a powerful electromeric effect, and it may be supposed that the chelation process sets up a demand upon the electrons of the nitrogen which causes this effect so to operate that the loss of negative charge by the reactive part of the complex is more than counteracted.—The Technical College, Cardiff. [*Received, June 15th*, **1939**.]

Amphiporine, an Active Base from the Marine Worm Amphiporus Lactifloreus. By Harold King.

Bacq (*Arch. Internat. Physiol.*, **1937**, **44**, 190), whilst examining marine animals at the Marine Biological Station at Plymouth for the presence of acetylcholine, found that the marine Nemertean worm, *Amphiporus lactifloreus*, contained a stable substance having a very powerful stimulating action on frog's voluntary muscle without the other characteristic properties of acetylcholine; other pharmacological properties were indistinguishable from those of nicotine. Micro-chemical tests carried out by the author on a portion of an alcoholic extract of 25 worms (each weighing less than 0·1 g.) showed that the active substance was a base which could be completely removed by extracting an alkaline solution with chloroform. Spot-tests with various reagents showed a close parallelism in properties with a dilute solution of nicotine.

Through the kind co-operation of the Director of the above laboratory, 1000 of these uncommon carnivorous worms were collected at low tide between October, **1936**, and February, **1938**, and kept in 90% alcohol. The solvent was decanted and the worms re-extracted with spirit after being ground with sand. The combined extracts were evaporated to a small volume under reduced pressure, acidified, and extracted with chloroform to remove fats and an orange pigment. The acid solution was made alkaline by adding sodium bicarbonate, and extracted with 4 portions of chloroform. The combined extracts were distilled, the residue being dissolved in 1 c.c. of N-hydrochloric acid (solution A). The bicarbonate mother-liquor was then made strongly alkaline with 50% sodium hydroxide (20 c.c.) and again extracted with chloroform, the residual base obtained on evaporating the solvent being dissolved in 2 c.c. of N-hydrochloric

acid (solution B). On the frog's *rectus abdominis*, A was highly active when diluted 1 : 1000, whereas B was inactive at this dilution, but slightly active at 1 : 10 dilution. Solution A was evaporated to dryness, the residual pale brown varnish weighing 44 mg. A 2% solution of this hydrochloride was compared, by spot-tests, with various standard precipitants, with a 2% solution of nicotine hydrochloride. The results of the tests preclude identity, for whereas the nicotine solution gave crystalline precipitates with solutions of picric acid, mercuric chloride, platinum chloride, flavianic acid, and ammonium reineckate, amphiporine hydrochloride solution gave an oily picrate,* a finely divided gummy mercury precipitate, a very fine microcrystalline chloroplatinate, an oily flavianate, and a partly crystalline reineckate. Accordingly, a larger proportion of amphiporine hydrochloride was precipitated with platinum chloride. Two crops, 6·5 and 5·6 mg., were obtained of granular, doubtfully crystalline material, both of which were unmelted at 310°. They were completely insoluble in boiling water or dilute acid, and all attempts to regenerate activity from them by metallic silver (Dudley, *Biochem. J.*, 1929, **23**, 1064) or by hydrogen sulphide were fruitless. This was apparently not due to destruction of the amphiporine, but to the unusual stability of the platinum complex. The mother-liquor from the chloroplatinates was also devoid of activity.

Although no sparingly soluble crystalline salt was discovered, suitable for characterising and purifying amphiporine for analysis, the parent aqueous hydrochloric acid solution on slow concentration to dryness, crystallised as a homogeneous mass of needles. The quantity was, however, insufficient for further purification.

I am indebted to Dr. Bacq, of Liége, for an opportunity of examining this interesting base, and to Dr. F. C. MacIntosh for comparing the activity of nicotine and amphiporine on the *rectus abdominis* of *Rana esculenta*. A 1 in 500,000 dilution of amphiporine exactly matched a 1 in 400,000 dilution of nicotine in this comparison.—NATIONAL INSTITUTE FOR MEDICAL RESEARCH, HAMPSTEAD, N.W. 3. [*Received, June 23rd*, 1939.]