Experimental

***o*-Nitromandelic Acid.**—A mixture of 7 g. of *o*-nitromandelonitrile and 110 ml. of concentrated hydrochloric acid was warmed to 70–80° under a reflux condenser for 20 hours. The resultant solution was then concentrated to a volume of 20 ml. under reduced pressure. The *o*-nitromandelic acid which had separated at this point was removed by filtration and the filtrate extracted twice with 30-ml. portions of ethyl acetate. The product obtained by filtration was dissolved in the ethyl acetate extracts, which were then dried over magnesium sulfate. Concentration and dilution of the hot solution with cyclohexane caused 5.1 g. of *o*-nitromandelic acid (64.5%), m.p. 137–138°, to be deposited as white crystals on cooling. Grillot and Bashford[4] report an identical melting point for this acid.

Reaction of *o*-Nitromandelic Acid with Formaldehyde and Piperidine.—This reaction was carried out exactly as described by Grillot and Bashford,[4] in order to ensure the identity of the product with that previously obtained. The once recrystallized material was dried over phosphorus pentoxide at reduced pressure and submitted for analysis, in order to confirm its empirical composition.

Anal. Calcd. for $C_{14}H_{20}O_6N_2$: C, 53.75; H, 6.40; N, 8.89. Found: C, 54.20; H, 6.33; N, 8.84.

The melting point of this product did not seem to be a reliable criterion of purity, since it was found to be strongly dependent on the rate of heating. Thus, using a Fisher melting point block, a high rate of heating caused the crystals to melt to a colorless liquid somewhere between 95–105°, whereas very slow heating resulted in some darkening with melting accompanied by decomposition occurring at 152–154°. It seems clear that the rapid heating gives the true melting point of the compound under consideration, while prolonged heating must result in some chemical change. It is perhaps worth noting in passing that repeated recrystallization led to the loss of some of the formaldehyde, with a resultant shift of the infrared spectrum toward that of piperidinium *o*-nitromandelate, and a parallel increase in apparent molecular weight.

Acid Treatment and Recovery of *o*-Nitromandelic Acid.—A 204-mg. sample of twice recrystallized "Mannich base" was dissolved in 5 ml. of water and the solution acidified with 3 drops of concentrated hydrochloric acid. The acidic solution was extracted rapidly with four 5-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and evaporated. The residue consisted of 125 mg. (94.6%) of *o*-nitromandelic acid, identified by melting point, mixture melting point and a comparison of its infrared absorption spectrum with that of an authentic sample.

Molecular Weight.—The cryoscopic measurements were made using a cell similar to that described by Billings,[8] but using a Western Electric 14B thermistor[9,10] for measuring temperature instead of a Beckmann thermometer. The thermistor circuit was similar to that used by Zemany[11] but somewhat modified to attain the desired precision. The resistance of the thermistor was measured with a Wheatstone bridge, employing a G.E. Photoelectric Recorder for the galvanometer. The apparatus was calibrated against a platinum resistance thermometer and the slope of the curve (in this case 0.00343° per ohm) used in calculating ΔT. The apparatus and method will be discussed fully in a later paper.

Two runs were made, each time diluting to obtain a second concentration. The material for the two runs was obtained from two separate preparations. The results are given in Table I.

TABLE I

APPARENT MOLECULAR WEIGHT OF "MANNICH BASE"

Run	I	Ia	II	IIa
Wt. sample, g.	0.299	0.299	0.192	0.192
Wt. water, g.	19.9	29.9	19.9	29.9
F.p. water, ohms	6441.5	6441.5	6441.5	6441.5
F.p. solution, ohms	6520.0	6593.5	6487.0	6471.0
$\Delta\Omega$	78.5	52.0	45.5	29.5
Apparent mol. wt.	104	104	115	118

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[8] O. B. Billings, Ph.D. Thesis, Cornell University, 1942.

[9] A thermistor is a ceramic resistor having a 4% change in resistance per degree change in centigrade temperature.

[10] K. P. Dowell, Electrical Manufacturing, August, 1948.

[11] P. D. Zemany, *Anal. Chem.*, **24**, 348 (1952).

The Properties of Nickel Carbide

BY G. MEYER AND F. E. C. SCHEFFER

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Browning and Emmett have published[1] a series of equilibrium measurements of the system Ni–C–H_2 and described some properties of a nickel carbide.[1] In their opinion their results disagree with those mentioned in a recent publication.[2]

In the latter a carbide is described which is exothermic (forms from the elements with evolution of heat). Below 419° this carbide is stable, at 700° it decomposes into its elements.[3] The carbide found by Browning and Emmett has quite different properties being endothermic. This follows from the lines of equilibrium in the diagram log *p versus* $1/T$ for the reaction with carbide and the reaction with carbon. These lines intersect at approximately 510°. Thus their carbide is stable above 510°, below this temperature there will be decomposition in carbon and nickel, the compound being unstable. The foregoing is proved by the free energy calculations made by the authors. For the reaction of formation of nickel carbide they find 7127 cal. at 500°K. and 4655 cal. at 600°K. These values being positive the carbide is metastable at these temperatures. Above approximately 783°K. (510°) the value for the free energy of formation becomes zero, the carbide being stable at higher temperatures. So the experiments of Browning and Emmett prove the existence of another carbide, quite different from the carbide described by us 25 years ago. The chemical composition of each carbide is unknown. Bahr and Bahr[4] propose the formula Ni_3C; from their work it is impossible to say whether the carbide they have obtained is the endothermic or the exothermic compound.

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[1] L. C. Browning and P. H. Emmett, THIS JOURNAL, **74**, 1680 (1952).

[2] F. E. C. Scheffer, T. Dokkum and J. Al, *Rec. trav. chim.*, **45**, 803 (1926).

[3] G. Meyer and F. E. C. Scheffer, *ibid.*, **46**, 1 (1927).

[4] H. A. Bahr and Th. Bahr, *Ber.*, **61**, 2177 (1928).

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11-Oxygenated Steroids. III. The Preparation of 11β-Hydroxy Pregnanes[1]

BY EUGENE P. OLIVETO, TEMPLE CLAYTON AND E. B. HERSHBERG

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The reported efficacy[2] of 17α-hydroxycorticosterone (Kendall's Compound F) in certain types of arthritis led us to prepare a series of 11β-hy-

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[1] For the previous paper in this series, *cf.* H. L. Herzog, M. A. Jevnik and E. B. Hershberg, THIS JOURNAL, **75**, 269 (1953).

[2] J. L. Hollander, *J. Am. Med. Assoc.*, **147**, 1629 (1951).