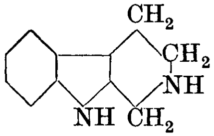
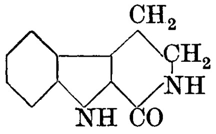
NOTES.

3 : 4 : 5 : 6-*Tetrahydro*-4-*carboline*. By JULIUS NICHOLSON ASHLEY and ROBERT ROBINSON.

3 : 4 : 5 : 6-TETRAHYDRO-4-CARBOLINE (tetrahydronorharman) (I) has been obtained by Asahina, Irie, and Ohta (*J. Pharm. Soc. Japan*, 1927, No. 545) by the reduction of a degradation product of evodiamine. The substance can also be readily prepared by the reduction of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (II) by means of sodium and *n*-butyl alcohol.

(I.)





(II.)

Experimental.—β-3-Indolylpropionhydrazide, m. p. 140—141°, and 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline, m. p. 185—186°, were readily obtained in satisfactory yield by the methods of Manske and Robinson (J., 1927, 240), but the melting points formerly ascribed to these substances are about 10° too low, evidently as the result of an unsuspected gross error in the thermometer, since the original specimens have been re-examined and found to melt at 140—141° and 185—186°, respectively.

Sodium (10 g.) was gradually added to a boiling solution of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (4 g.) in *n*-butyl alcohol (100 c.c.). After 2 hours' refluxing, 90% alcohol (100 c.c.) and water (100 c.c.) were successively introduced and the mixture was distilled in a current of steam. The pale brown residue in the flask crystallised from alcohol (charcoal) in colourless, elongated prisms, m. p. 204° (Found : C, 76·6; H, 7·0; N, 16·5. Calc. for $C_{11}H_{12}N_2$: C, 76·7; H, 7·0; N, 16·3%). The salts of the base are readily soluble in water and the nitroso- and acetyl-derivatives are insoluble in dilute hydrochloric acid. The picrate crystallises from acetone-alcohol in bright canary-yellow, prismatic needles, m. p. 249—251° (decomp.). Asahina, Irie, and Ohta (*loc. cit.*) state that their base, $C_{11}H_{12}N_2$, has m. p. 204—205° (picrate, m. p. 250—251°).

On oxidation of the base with chromic acid in hot dilute sulphuric acid, norharman was obtained in poor yield; after purification, this had m. p. 198°, not depressed on admixture with an authentic specimen.—THE UNIVERSITY, MANCHESTER. [*Received*, *April* 11*th*, 1928.]

The Occurrence of Titanium Tetrachloride in Commercial Disilicon Hexachloride. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON.

IN the course of some experiments with disilicon hexachloride, which was kindly supplied by Messrs. Albright and Wilson, it was observed that the addition of 0·3—0·5 c.c. of the hexachloride to purified ether (100 c.c.) caused the development of a yellow colour; this occurred not only with the crude material, but also—although in a less marked manner—with samples which had been fractionated twice through a 12-inch rod and disc column, boiled at 145—147°, and contained Cl 78·7% (Si_2Cl_6 requires 78·9%). When, on the other hand, about 1 c.c. of ether was added to the fractionated hexachloride (100 c.c.) there was an immediate precipitation of a small proportion of a yellow, crystalline substance. This product melted at 42—45° and was doubtless identical with the compound $TiCl_4,(C_2H_5)_2O$ which Bedson obtained by the direct combination of titanium tetrachloride and ether (J., 1876, **29**, 311). The presence of titanium tetrachloride in the disilicon hexachloride was also proved by the hydrogen peroxide reaction, and with thymol and sulphuric acid; by reduction and titration with iron alum its quantity in the twice fractionated sample was found to be 1·6%. For the complete separation of the titanium tetrachloride (b. p. 135°) from the disilicon hexachloride (b. p. 147°) repeated fractionation through a rod and disc column is necessary; after five or six operations the hexachloride gives no colour reaction with hydrogen peroxide solution.

The compound $TiCl_4,(C_2H_5)_2O$ (b. p. 118—120°) cannot be easily separated from the disilicon hexachloride by distillation; when it is decomposed by alkali and the aqueous solution is then distilled, the distillate gives a distinct iodoform reaction.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 24th,* 1928.]

Fission of the Pyridine Nucleus by Oxidation with Alkaline Potassium Permanganate. By BRIAN DUNCAN SHAW and ARTHUR LESLIE WILKIE.

THE fact that the pyridine nucleus can be ruptured by the action of either acid or alkaline permanganate was observed by one of us (B. D. S.) in 1921. The results with the former reagent agreed entirely with the observations of Delépine (*Compt. rend.*, 1927, **184**, 206). A more extended investigation of the action of alkaline permanganate was commenced, but as one of us has been obliged to abandon the work, the initial results are now given.

Pure pyridine (5 g.) was boiled with water (250 c.c.), and finely powdered potassium permanganate added in quantities of 5 g. at a time until a permanent pink colour resulted (50 g. during 12 hours). The odour of pyridine had then vanished. A deposit of ammonium carbonate appeared in the condenser during the first hour. The manganese dioxide was removed, and the filtrate evaporated to dryness. The white, deliquescent residue was a mixture of the potassium salts of carbonic, oxalic, nitric and nitrous acids. The quantity of potassium permanganate used was only about two-thirds of that calculated from the equation $2C_5H_5N + 11O_2 = 10CO_2 + 2NH_3 + 2H_2O$.

The fact that the nucleus itself is attacked by alkaline permanganate accounts for the low yields of pyridinecarboxylic acids, obtained by the oxidation of side chains with this reagent, when the solution is overheated.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March* 31*st*, 1928.]

The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. By ERWIN OTT.

Two communications bearing the title of this note (Lunt and Venkataswaran, J., 1925, **127**, 2052; 1927, 857) make it necessary to point out that experiments treating the same subject have been published by me (*Ber.*, 1925, **58**, 772). My results, however, are not in harmony with those of the two authors, who give for the decomposition of the carbon monoxide the equation $7CO = C_5O_3 + 2CO_2$, and for the brown solid the formula C_5O_3,xH_2O. By quantitative investigations of a different kind, and by definite evidence of the production of unimolecular C_3O_2 in the gases leaving the Siemens ozoniser, I showed that the equation of the decomposition is $4CO = C_3O_2 + CO_2$, and that the brown solid is the product of polymerisation of gaseous C_3O_2.—THE UNIVERSITY, MÜNSTER (WESTFALIA), GERMANY. [*Received, April* 2*nd*, 1928.]

Separation of Phthalic and Homophthalic Acids. By HARRY GORDON POOLE.

FOR the recovery of homophthalic acid from residues containing much phthalic acid, crystallisation is an unsatisfactory method. Practically complete separation is achieved, however, by means of the great difference in solubility of copper phthalate (Hermann, *Annalen*, 1869, **151**, 78), which is soluble in about 30 parts of water at 30°, and *copper homophthalate*, the solubility of which in water is less than 0·02% (1 part in 5000) at 25° and less than 0·01% at 100°.

The homophthalate is precipitated from mixed solutions of copper sulphate and sodium homophthalate in greenish-blue, microscopic crystals which, owing to their insolubility in ordinary neutral organic solvents, are difficult to obtain in a perfectly pure condition (Found : Cu, 25·3. $C_9H_6O_4Cu$ requires Cu, 26·2%). They readily become electrified when rubbed with a glass rod.

In order to separate homophthalic acid from phthalic acid, the mixture is neutralised with sodium hydroxide and diluted considerably, and a solution of copper sulphate is added in the cold. (If a solution of copper phthalate containing copper sulphate is boiled, a greenish-blue, flocculent precipitate, apparently of a basic salt, is formed.) After 12 hours the flocculent precipitate is filtered off, washed, and treated with concentrated hydrochloric acid and sufficient water to dissolve the mass on boiling. The homophthalic acid separates on cooling, in good crystals having the correct melting point, 181°. From an artificial mixture of phthalic acid (66·6%) and homophthalic acid (33·3%), 90% of the homophthalic acid was recovered in this way.—UNIVERSITY OF MELBOURNE. [*Received, April* 11*th*, 1928.]