NOTES.

The Nature of the Deposit formed during the Electrolysis of Neutral and Alkaline Solutions with an Antimony Cathode. By JULIUS GRANT.

ACCORDING to Weeks and Druce (J., 1925, **127**, 1069) a solid hydride of antimony (Sb_2H_2) is produced when stibine is passed into a concentrated solution of sodium hydroxide, and the black deposit found on the bottom of the cell after the electrolysis of such a solution with an antimony cathode is ascribed to the same reaction. In the course of some earlier investigations (*Trans. Faraday Soc.*, in the press) fifteen of these deposits, produced under widely varying conditions, were examined. They included those produced (i) in the cathode compartment and on the cathode after electrolysis of (*a*) sodium hydroxide solutions (0·05—3*N*) with an antimony cathode, (*b*) solutions containing suspended metallic antimony or its compounds with a lead cathode, and (ii) by reduction of antimony compounds with nascent hydrogen. The anode was platinum and the current densities varied from 1 to 4 amps./cm.^{2}.

The deposits were filtered off, washed free from alkali, and dried as rapidly as possible by alcohol and ether, or by prolonged desiccation, and analysed by the measurement, using a Töpler pump, of the volume of hydrogen from 10 mg. liberated in a vacuum at a bright red heat. The amount of gas obtained varied from 0·01 to 0·25%, and was usually 0·1%. It burnt in a manner similar to hydrogen, but was not otherwise examined.

Since the compound Sb_2H_2 would contain 0·83% of hydrogen, it seems probable that the deposits consisted of metallic antimony in a finely divided state, with small traces of adsorbed hydrogen which is removed only by the effect of heat at a low pressure. Further, the deposits resembled finely powdered pure metallic antimony both in appearance and in chemical properties, whereas those of antimony hydride behave quite differently (Weeks and Druce, *loc. cit.*). The deposits are produced by decomposition of the electrolytic stibine and not by cathodic disintegration, since they are obtained even with lead cathodes, and whereas the yield of stibine (calculated from the sum of that evolved as gas and that decomposed into metal and hydrogen) varies regularly with variations in the conditions of electrolysis, the relative proportions obtained in the form of gas or deposit are dependent only on the structure of the apparatus (Sand, Grant, and Lloyd, J., 1927, 378).—SIR JOHN CASS TECHNICAL INSTITUTE, LONDON, E.C.3. [*Received, May* 16*th*, 1928.]

NN′-*Diphenyl*-o-*phenylenediamine*. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

FROM *o*-aminodiphenylamine and iodobenzene in boiling nitrobenzene solution, Wieland and Müller (*Ber.*, 1913, **46**, 3303) obtained a substance, m. p. 152·5°, which they described as *NN′*-diphenyl-*o*-phenylenediamine, $C_6H_4(NHPh)_2$. Clemo, Perkin, and Robinson (J., 1924, **125**, 1780 : errata, p. 2796) condensed 2′-aminodiphenylamine-6-carboxylic acid with *o*-chlorobenzoic acid and distilled the resulting 2′-*o*-carboxyphenylaminodiphenylamine-6-carboxylic acid; loss of carbon dioxide then took place and the product melted at 109°. They described this as *NN′*-diphenyl-*o*-phenylenediamine and suggested that the compound obtained by Wieland and Müller was not this substance but the isomeric *o*-aminotriphenylamine, $NH_2{\cdot}C_6H_4{\cdot}NPh_2$. This suggestion is correct.

On carrying out the preparation described by Wieland and Müller, the product obtained had m. p. 149—150° and behaved like a primary amine towards nitrous acid. The monoacetyl derivative, prepared by boiling this substance for 15 minutes with an excess of acetyl chloride, had m. p. 131—132° after recrystallisation from aqueous alcohol (Found : N, 9·4. Calc. : N, 9·3%). *o*-Aminotriphenylamine was prepared by the method of Piccard and Brewster (*J. Amer. Chem. Soc.*, 1921, **43**, 2630). This and the corresponding monoacetyl derivative proved to be identical with Wieland and Müller's supposed *NN′*-diphenyl-*o*-phenylenediamine and its monoacetyl derivative respectively. *o*-Nitrotriphenylamine (Piccard and Larsen, *J. Amer. Chem. Soc.*, 1917, **39**, 2006), crystallised from ligroin (b. p. 60—80°), had m. p. 100°.

For the purposes of another investigation, we have prepared *NN′*-diphenyl-*o*-phenylenediamine in quantity by the method of Clemo, Perkin, and Robinson and through the kindness of these authors have been able to compare the final and intermediate compounds with original specimens.

In the condensation of *o*-aminodiphenylamine with iodobenzene it is therefore the secondary amino-group which is the more reactive, but in the condensation of 2′-aminodiphenylamine-6-carboxylic acid it is the primary amino-group which reacts. It is suggested that in the latter case the activity of the secondary amino-group is diminished or inhibited by internal salt formation with the adjacent carboxyl group.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), S.E.1. [*Received, May 15th*, 1928.]

The Action of Disilicon Hexachloride on Ether. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON.

IT has been shown by Kipping and Murray (J., 1927, 2734) that ether reacts with silicon tetrachloride to a slight extent, giving some compound from which alcohol is produced on treatment with aqueous alkali. Disilicon hexachloride seems to behave in a similar manner.

A sample of the hexachloride (5—6 g.), carefully freed from titanium tetrachloride (this vol., p. 1377), was left in contact with about 10 volumes of ether. (The latter had been purified with sodium and by leaving it in contact with disilicon hexachloride during a week; it gave no reaction for alcohol.) Most of the ether was then distilled on the water-bath, excess of sodium hydroxide solution was added to the residue, and 4—5 c.c. of the aqueous solution distilled; the distillate gave with iodine and alkali a distinct precipitate of iodoform. The ether recovered from the first distillation was again mixed with the hexachloride, and the above operations repeated; iodoform was again obtained, and a further experiment with the same ether gave a like result. The quantity of iodoform produced in each experiment was only a few milligrams and was not appreciably increased by gently heating the mixture of the two substances: it seems, therefore, that the interaction is very limited, as in the case of silicon tetrachloride and ether.

It may be suggested that both the silicon chlorides form with ether additive products, corresponding with the compound $TiCl_4,Et_2O$ (Bedson, J., 1876, **29**, 311), and that these decompose at the ordinary temperature, or when they are gently heated, with formation of ethyl chloride and chloroethoxysilicon derivatives which are analogous to Bedson's titanium compound, $TiCl_3{\cdot}OEt$.

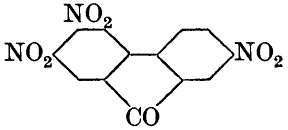
A sample of the silicon tetrachloride which had been used by Kipping and Murray in their experiments with ether was proved to have been free from titanium tetrachloride.—University College, Nottingham. [*Received, June 6th,* 1928.]

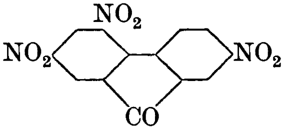
---

2 : 4 : 7-*Trinitrofluorenone.* By Frank Bell.

The interest attaching to heavily substituted fluorenones (Bell and Robinson, J., 1927, 1695) directed attention to the statement that fluorenone on nitration yields the 2 : 3 : 7-trinitro-derivative (I) (Schmidt and Bauer, *Ber.*, 1905, **38**, 3758). Apart from the exceptional orientation of this compound, its oxidation to yield 3 : 4-dinitrobenzoic acid called for further examination (for normal method of oxidation of fluorenone derivatives, see Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 1324).

(I.)





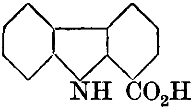
(II.)

4-Nitrofluorenone, prepared from 4-nitrophenanthraquinone (Schmidt and Bauer, *ibid.*, p. 3741; Morgan and Thomason, J., 1926, 2695), was nitrated as follows: 1·25 g. in nitric acid (*d* 1·5; 25 c.c.) were warmed on a steam-bath for 2 hours, cooled, and poured into water. The precipitate after several crystallisations from benzene had m. p. 175° (Found: C, 49·5; H, 1·6. $C_{13}H_5O_7N_3$ requires C, 49·5; H, 1·6%). This trinitro-derivative must therefore be 2 : 4 : 7-*trinitrofluorenone* (II).

Fluorenone nitrated by the method of Schmidt and Bauer (*loc. cit.*) gave a product, m. p. 176° after repeated crystallisation from acetic acid or benzene (Found: C, 49·9; H, 1·8%). When mixed with the 2 : 4 : 7-trinitrofluorenone described above, it melted at the same temperature. Oxidation of this trinitro-derivative gave a very small amount of an impure acid, m. p. 165—170°. The m. p. of the purified acid would obviously exceed that of 3 : 4-dinitrobenzoic acid (164°).—Battersea Polytechnic, S.W.11. [*Received, June 8th,* 1928.]

Carbazole-1-*carboxylic Acid.* By Edward Fuller Briscoe and Sydney Glenn Preston Plant.

The proof, hitherto lacking, that the acid obtained by the action of carbon dioxide on potassium carbazole at 270° (Ciamician and Silber,



Gazzetta, 1882, **12**, 272) or on magnesium 9-carbazyl iodide at 265—270° (Oddo, *ibid.*, 1911, **41**, i, 255) is carbazole-1-carboxylic acid, has now been furnished by boiling a mixture of tetrahydrocarbazole-8-carboxylic acid (Collar and Plant, J., 1926, 808) (12 g.), sulphur (3 g.), and pure quinoline (80 c.c.) under reflux for 12 hours and then pouring it on ice–dilute hydrochloric acid. The sticky product was dissolved in dilute aqueous sodium hydroxide, and the solution was boiled with charcoal, filtered, and acidified with hydrochloric acid. The crude acid was dried and then boiled for 6 hours with methyl-alcoholic hydrogen chloride. The methyl ester, obtained by pouring the solution into dilute ammonia, was distilled under reduced pressure, further purified by crystallisation from aqueous alcohol, and then hydrolysed with methyl-alcoholic sodium hydroxide. After recrystallising twice from toluene–petroleum, the resulting acid was obtained in yellowish plates, m. p. 268—269° (Found: C, 73·8; H, 4·5. Calc.: C, 73·9; H, 4·3%), which did not depress the m. p. (270—271°) of a specimen of carbazole-1-carboxylic acid prepared by the method of Ciamician and Silber.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, June* 22*nd*, 1928.]