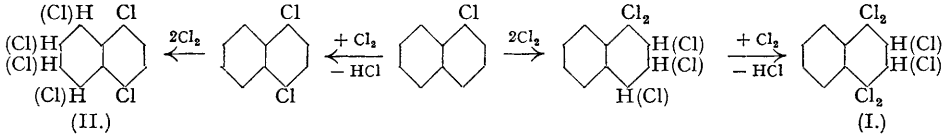
# NOTES.

**1 : 2 : 3 : 4-*Tetrachloronaphthalene*.** By W. PALMER WYNNE.

IN their paper on tetrachloronaphthalenes derived from dichloronaphthalene tetrachlorides, Turner and Wynne (*J.*, 1941, 245) described an isomer (I), m. p. 157°, of Widman's 1 : 4-dichloronaphthalene tetrachloride (II), m. p. 172°, obtained from 1-chloronaphthalene not as was his compound by the passage of chlorine into its solution in chloroform, but from it or its tetrachloride (m. p. 131°) in carbon disulphide solution by saturation with chlorine, preferably in sunlight. Whereas, by interaction with alcoholic sodium hydroxide, Widman's product furnished 1 : 3 : 5 : 8-tetrachloronaphthalene, m. p. 131°, the isomer (I) yielded a tetrachloro-derivative, m. p. 196°, of unknown constitution which at the time was thought to be new. Unfortunately, the fact that von Braun *et al.* (*Ber.*, 1923, **56**, 2337 footnote) had prepared a compound, m. p. 198°, described as 1 : 2 : 3 : 4-tetrachloronaphthalene, from 1′ : 2′ : 3′ : 4′-tetrachlorotetralin was overlooked. By repetition of their method, the identity of the two products has been established. The relationship between (I) and (II) is shown in the scheme




(II.) (I.)

Some details may be added to those very briefly mentioned in von Braun's footnote. In the first place, no specific reference is made to the addition of iodine to the tetralin before exhaustive chlorination; without it, a thick, non-crystallisable syrup is the product. The yield of 1′ : 2′ : 3′ : 4′-tetrachlorotetralin, m. p. 174°, averaged 20 g. from 63 g. of highly purified tetralin. Conversion of the tetrachloro-compound (5 g.) into the dibromo-derivative by the addition of bromine (6 g.) to its solution in boiling carbon disulphide, as prescribed, gave an unsatisfactory product, but in acetic acid at the boiling point for half an hour, a uniform separation of tetrachlorodibromotetralin (2·4 g. from 5 g.) either in flat rhombs with a diagonal extinction or in monoclinic prisms, m. p. 146° (von Braun *et al.*, m. p. 142°), was obtained. When the temperature was raised slowly in the usual way, it melted at *ca.* 135° (decomp.) but, if introduced into the bath at temperatures between 135° and 147°, it remained solid for a short time and only at 146—147° did it melt sharply (Found: C, 28·1; H, 1·4; hal., 70·6. Calc. for $C_{10}H_6Cl_4Br_2$: C, 28·1; H, 1·4; hal., 70·5%). The tetrachloronaphthalene from this source had m. p. 196°, did not depress the m. p. of T. and W.'s product and like the latter, when heated with nitric acid (*d* 1·16) at 210—215° under pressure during not more than 10 minutes, gave an acid the dimethyl ester of which had the m. p. 92° found by Graebe for dimethyl 1 : 2 : 3 : 4-tetrachlorophthalate (*Annalen*, 1905, **340**, 247).

The suggestion that Atterberg and Widman's [δ-] tetrachloronaphthalene, m. p. 141° (*Ber.*, 1877, **10**, 1842) might be identical with the 1 : 2 : 3 : 5-derivative (T. and W., *loc. cit.*, p. 244, footnote; the m. p. 144° in the table on p. 247 is a misprint for 141°) has been confirmed by a repetition of their work. When a solution of 1 : 5-dichloronaphthalene (31 g.) in chloroform was saturated with chlorine, the dichloronaphthalene tetrachloride, m. p. 84° (5·7 g.) and trichloronaphthalene dichloride, m. p. 94° (10·8 g.)—separated by the sparing solubility of the latter in methanol—were obtained and both gave the product, m. p. 141°, by interaction with alcoholic sodium hydroxide. By contrast, when 2 : 6-dichloronaphthalene dissolved in chloroform was saturated with chlorine under comparable conditions, the only product isolated was the substitution derivative, 1 : 2 : 6-trichloronaphthalene, m. p. 92° in small yield (5·3 g. from 47·5 g.; Found: Cl, 45·8. Calc. for $C_{10}H_5Cl_3$: Cl, 46·0%).

The author's thanks are due to Imperial Chemical Industries (Billingham Division) Ltd., for a gift of highly purified tetralin and to Mr. F. C. Baker of this laboratory for help in the experimental work.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, October 30th*, 1945.]

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***Quinolyl Derivatives of* p-*Aminobenzamide*.** By JOHN H. GORVIN.

THREE p-*aminobenzamidoquinolines* have been prepared by reduction of the corresponding *nitro*-compounds obtained by interaction of *p*-nitrobenzoyl chloride with 5-aminoquinoline, 8-aminoquinoline and 8-amino-6-methoxyquinoline respectively. They have been tested for antimalarial or trypanocidal action by Mr. L. G. Goodwin and Dr. P. B. Marshall, but show no appreciable activity against *Plasmodium gallinaceum* in chicks or *Plasmodium cathemerium* in canaries, or against *Trypanosoma equiperdum* and *Trypanosoma cruzi* in mice. Dr. G. Brownlee of the Wellcome Physiological Research Laboratories has found them to be inactive against streptococcal infections in mice.

*Preparation of the* p-*Nitrobenzamidoquinolines*.—To a mechanically stirred solution of *p*-nitrobenzoyl chloride (1 mol.) in dry ether was slowly added the appropriate aminoquinoline (1 mol.) dissolved in the same solvent. The precipitated orange-yellow hydrochloride was separated after 30 minutes. It was washed with dry ether and decomposed with aqueous ammonia. The crude product (75—85%) was purified by recrystallisation from glacial acetic acid. In this way were prepared: 5-p-*nitrobenzamidoquinoline*, pale yellow crystalline powder, m. p. 267—268·5° (Found: C, 65·6; H, 3·9; N, 14·2. $C_{16}H_{11}O_3N_3$ requires C, 65·5; H, 3·8; N, 14·2%); 8-p-*nitrobenzamidoquinoline*, small golden needles, m. p. 188° (Found: C, 65·6; H, 3·9; N, 14·4%); 8-p-*nitrobenzamido*-6-*methoxyquinoline*, orange-yellow felted needles, m. p. 241° (Found: C, 63·4; H, 4·5. $C_{17}H_{13}O_4N_3$ requires C, 63·2; H, 4·1%).

*Reduction of the* p-*Nitrobenzamidoquinolines*.—For the reduction of the 5-isomeride, iron filings (7·5 g.) and 5% aqueous acetic acid (25 c.c.) were warmed to 95° on a water-bath and the nitro-compound (5 g.) added in small portions. After heating for an hour the mixture was made alkaline and filtered. The dry solid residue was extracted with ethanol in a Soxhlet apparatus, and the crude 5-p-*aminobenzamidoquinoline* (2·6 g., 59%) was recrystallised from the same solvent to give prisms, m. p. 264—265° (Found: C, 73·2; H, 5·0. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 5·0%).

The reduction of the other two nitro-compounds was carried out by hydrogenation in glacial acetic acid in presence of Adams's platinum oxide catalyst. The reaction was slow at ordinary temperature and pressure, but proceeded to completion to give 8-p-*aminobenzamidoquinoline*, needles from aqueous ethanol, m. p. 184° (Found: C, 72·7; H, 5·0. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 5·0%) and 8-p-*aminobenzamido*-6-*methoxyquinoline*, needles from aqueous ethanol, m. p. 213—214° (Found: C, 69·7; H, 5·2. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·2%). Hydrogenation of 5-*p*-nitrobenzamidoquinoline was impeded by the separation of a highly insoluble intermediate compound, m. p. *ca.* 350°.

All m. ps. are corrected.

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*The Diethylaminoalkylation of* 9-*Amino*-p-*phenanthroline.* By Rex G. Jacomb and William O. Kermack.

When 9-amino-*p*-phenanthroline (7-amino-6 : 5 : 2′ : 3′-pyridoquinoline), prepared by the method of Haworth and Sykes (*J.*, 1944, 311), was treated with diethylaminoethyl chloride hydrochloride under various conditions, either no reaction took place or a deeply coloured product was obtained from which dilute alkali precipitated no base but strong alkali precipitated a tarry product. It appeared that one of the nuclear nitrogen atoms had reacted yielding quaternary salts. Haworth and Sykes found that the 9-acetamido-*p*-phenanthroline very readily formed a monomethiodide whereas the analogous acetamido-*m*-phenanthroline yielded metho salts only with difficulty. This formation with difficulty of quaternary salts in the *m*-phenanthroline series is in conformity with the fact that, according to E.P. 454525, the amino-*m*-phenanthroline yields diethylaminoalkylamino-*m*-phenanthroline when heated with the appropriate diethylaminoalkyl chloride hydrochloride. Dewar (*J.*, 1944, 619) describes the alkylaminoalkylation of various aromatic amines in toluene solution in presence of sodamide; the application of this method to 9-amino-*p*-phenanthroline avoided the formation of quaternary compounds and gave the desired diethylaminoalkylamino derivatives. By following Dewar's instructions, the yield was poor, much of the unchanged starting material being recovered. An attempt to speed up the reaction by carrying it out in boiling xylene instead of toluene was unsuccessful; at the higher temperature more rapid reaction obviously took place, but a highly coloured product was obtained as in the earlier experiments in the absence of sodamide, and it appeared that quaternary salt formation had again taken place. However, prolonged treatment with extra sodamide and diethylaminoalkyl chloride much improved the yield. In this way were obtained 9-*γ*-diethylaminopropylamino-*p*-phenanthroline and 9-*β*-diethylaminoethylamino-*p*-phenanthroline, both oils conveniently isolated and purified through their crystalline 3 : 5-*dinitrobenzoates*. All attempts to obtain such bases by condensing 9-bromo-*p*-phenanthroline and diethylaminoalkylamines were unsuccessful.

9-*γ*-*Diethylaminopropylamino*-p-*phenanthroline*. 9-Amino-*p*-phenanthroline (2 g.), toluene (30 c.c. distilled and dried over sodium wire), sodamide (0·5 g.) and *γ*-diethylaminopropyl chloride (1·5 g., freshly distilled in a vacuum) were refluxed in an oil bath for 18 hours with the addition, every 6 hours, of sodamide (0·2 g.) and *γ*-diethylaminopropyl chloride (0·8 g.) making a total of sodamide (0·9 g.) and *γ*-diethylaminopropyl chloride (3·1 g.). After standing overnight the mixture was filtered from a small amount of sodium chloride and the filtrate extracted with 15% acetic acid. The red (green fluorescence) extract was made alkaline with 10N-sodium hydroxide solution and extracted with ether. On drying (sodium sulphate) and removal of the ether, the resulting brown oil was kept for ½ hour under reduced pressure at 100° to remove traces of *γ*-diethylaminopropyl chloride. To a solution of the residual base in alcohol (*ca.* 5 c.c.) was added a saturated alcoholic solution of 3 : 5-dinitrobenzoic acid. The 3 : 5-*dinitrobenzoate* which separated as an oil, crystallised overnight; it was obtained as oblong prisms (5·2 g.), m. p. 172° after repeated crystallisation from hot water. (Dried at 80° in a vacuum over phosphorus pentoxide; found: C, 53·6; H, 4·2; N, 15·1. $C_{19}H_{22}N_4,2C_7H_4O_6N_2,\frac{1}{2}H_2O$ requires C, 53·5; H, 4·4; N, 15·1%. Dried at 120° in vacuum; found: C, 53·80; H, 4·1. $C_{19}H_{22}N_4,2C_7H_4O_6N_2$ requires C, 54·1; H, 4·4%).

9-*β*-Diethylaminoethylamino-*p*-phenanthroline was prepared similarly from 9-amino-*p*-phenanthroline and *β*-diethylaminoethyl chloride. The oily product, dissolved in alcohol, was converted into the 3 : 5-*dinitrobenzoate*. It crystallised from hot water as yellow needles, m. p. 173°, and was dried at 80° under reduced pressure over phosphorus pentoxide (Found: C, 49·7; H, 3·7; N, 14·4. $C_{18}H_{22}N_4,3C_7H_4O_6N_2,H_2O$ requires C, 49·3; H, 3·8; N, 14·8%).—Research Laboratory, Royal College of Physicians, Edinburgh. [*Received, November 2nd*, 1945.]