69. *Derivatives of Methylene-blue.*

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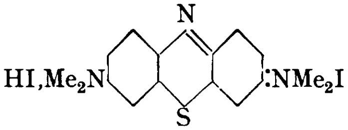
Although methylene-blue may become *p*-quinonoid (see Kehrmann; MacNeal and Killian, *J. Amer. Chem. Soc.*, 1926, **48**, 740) there seems to be no evidence that it is capable of assuming the *o*-quinonoid form. This form has two side-chain nitrogen atoms which might become quaternary, whereas the *p*-quinonoid form has only one. By treating the *iodide* of methylene-blue with methyl iodide in methyl alcohol, however, we failed to obtain any quinonoid methiodides of methylene-blue, the only methiodides produced being derivatives of the leuco-compound. Two crystalline quinonoid derivatives were obtained, which proved to be the mono- and the di-hydriodide of methylene-blue iodide: it is difficult to represent the latter otherwise than as *o*-quinonoid.

When methylene-blue iodide was refluxed with a large excess of methyl alcohol and methyl iodide, *methylene-blue iodide monohydriodide* (I or II) separated in purple-black crystals and *leucomethylene-blue dimethiodide* (III) remained in the mother-liquor. The yield of (I) was about 90% when 15 volumes of methyl alcohol to one volume of methyl iodide were used, and fell to about 50% with half the proportion of methyl iodide; with methyl alcohol and methyl iodide in the proportion 4 : 3 and prolonged refluxing, the product isolated was almost wholly the leuco-derivative.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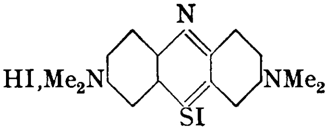
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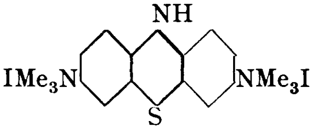
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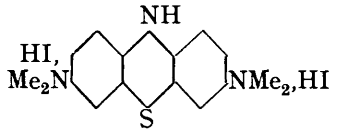
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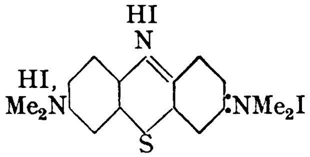
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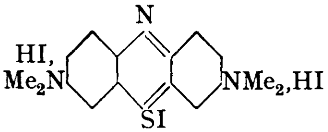
(VI.)

When ethyl alcohol and ethyl iodide were substituted for the methyl compounds, the volume of ethyl alcohol being ten times that of the ethyl iodide, (I) was again produced; but when the proportion was 5 : 3, iodine was liberated and about 75% of the methylene-blue iodide was converted into *leucomethylene-blue dihydriodide* (IV). This substance is very soluble in water and easily oxidised to the dye, whereas (III) is only moderately soluble in water and is not oxidised unless methyl iodide is first split off. Leucomethylene-blue diethiodide was not isolated.

It was clear that the methylating and ethylating mixtures were both acting as sources of hydrogen iodide, part of which reduced the methylene-blue iodide, the remainder being added to the dye. Alkylation of the alcohols to ethers is therefore probably the primary reaction in both cases. Further refluxing of (I) with ethyl alcohol and ethyl iodide gave rise to (IV).

The structure of (III) was confirmed by preparing it by the direct methylation of leucomethylene-blue with methyl iodide and methyl alcohol; that of (IV) by preparing it from methylene-blue iodide and ethyl-alcoholic hydrogen iodide; that of (I) by preparing it (1) by the addition of two atomic proportions of iodine to leucomethylene-blue dissolved in acetonitrile, and (2) by double decomposition in acetonitrile between methylene-blue iodide and its dihydriodide, a reaction which is reversed in methyl alcohol (see below):

$$C_{16}H_{19}N_3S + I_2 = C_{16}H_{18}N_3SI(HI) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$C_{16}H_{18}N_3SI + C_{16}H_{18}N_3SI(HI)_2 \underset{(CH_3\cdot OH)}{\overset{(CH_3\cdot CN)}{\rightleftharpoons}} 2C_{16}H_{18}N_3SI(HI) \quad . \; . \; . \quad (2)$$

From (IV) the hydrogen iodide was readily removable (*e.g.*, by means of pyridine) with the production of leucomethylene-blue.

In all the preparations of methylene-blue iodide monohydriodide from methyl-alcoholic methyl iodide and methylene-blue iodide, more than sufficient hydrogen iodide was theoretically available to convert the whole of the monohydriodide into a dihydriodide. The fact that this did not occur, whereas the dihydriodide of the leuco-compound is readily formed, is an argument in favour of formula (I) as against (II). Nevertheless, under other conditions (see later) the monohydriodide is readily transformed into a dihydriodide.

When the monohydriodide (I) was boiled with much methyl alcohol for some time, it gave approximately equimolecular proportions of methylene-blue iodide and *methylene-blue iodide dihydriodide* (V or VI). Repeated treatment with boiling water also transformed (I), though less smoothly, into the same two substances; so the reaction can be interpreted as a redistribution of hydrogen iodide (equation 2).

The constitution of the dihydriodide was confirmed (1) by its direct preparation (yield 75%) from hydrogen iodide and the monohydriodide in glacial acetic acid, and (2) by the addition of hydrogen iodide (1 *or* 2 mols.) to methylene-blue iodide in the same solvent, although, owing to reduction, the yield of dihydriodide was here only 50%. Further confirmation was supplied by the interaction, in acetonitrile solution, of methylene-blue iodide and the dihydriodide, which gave the monohydriodide in a yield of 70% (equation 2); and also by removing the hydrogen iodide from the dihydriodide, by means of quinoline, with production of methylene-blue iodide and quinoline hydriodide in approximately quantitative yields.

That no iodine is substituted in the aromatic nuclei is shown by the fact that phenylhydrazine reduces the iodide dihydriodide to leucomethylene-blue, with quantitative liberation of nitrogen:

$$C_{16}H_{18}N_3SI(HI)_2 + 4C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_6 + N_2 + 3C_6H_5{\cdot}NH{\cdot}NH_2(HI) + C_{16}H_{19}N_3S.$$

These facts, together with the analytical data, establish the relationship between methylene-blue iodide and the two hydriodides, in spite of the rather unexpected properties of the latter substances. For comparison, we examined the derivatives of Bindschedler's-green, in which the sulphur atom of methylene-blue is replaced by two hydrogen atoms, with marked diminution of the stability of the dye. Leuco-Bindschedler's-green, $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, is much more stable towards oxidising agents than is leucomethylene-blue, but, like the latter, it reacts with two atomic proportions of iodine to give *Bindschedler's-green iodide monohydriodide*, $HI,NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NMe_2I$, which was also prepared by the action of dilute methyl-alcoholic methyl iodide upon Bindschedler's-green iodide; it forms blue-black prisms, insoluble in water. There is thus complete analogy with methylene-blue as regards the iodide monohydriodide. Attempts to prepare an iodide dihydriodide, however, failed, a result which may be accounted for either by adopting (VI) as the formula for methylene-blue iodide dihydriodide or by assuming that the presence of the sulphur atom enhances the basicity of the central nitrogen atom in (V). The latter argument, however, is scarcely valid, since even thiodiphenylamine forms only unstable salts. Formula (VI) necessitates a change of *p*- to *o*-quinonoid structure in passing from the mono- to the di-hydriodide; but a simple mechanism is available for this change, in the addition of iodine and hydrogen, as ions, to sulphur and nitrogen, respectively. If this conclusion be correct, it follows from the experimental results that methyl alcohol and glacial acetic acid allow the production of *o*-quinonoid forms, whereas acetonitrile and methyl-alcoholic methyl iodide favour the *p*-quinonoid.

The possibility that the hydriodides of methylene-blue iodide may be (1) periodides or (2) salts of meriquinonoid type cannot be reconciled either with the analytical figures (particularly those for hydrogen) or with the various transformations already given.

Both hydriodides are stable substances, the crystals of which, unlike those of most (if not all) true periodides, exert no pressure of iodine vapour; they yield no alkali iodate when decomposed by hot aqueous caustic alkali; and free iodine cannot be obtained from them by any known means not involving oxidation. There seems no doubt, therefore, that they are hydriodides and not periodides.

It is concluded that the present work tends to support the hypothesis that methylene-blue may give rise under different conditions to both *p*- and *o*-quinonoid derivatives.

EXPERIMENTAL.

Methylene-blue iodide was prepared by the addition of an excess of KI to aq. methylene-blue chloride (Bernthsen, *Ber.*, 1883, **16**, 1025), crystallised several times from H_2O, and dried in vac. at 110° (Found: C, 45·8; H, 4·8. $C_{16}H_{18}N_3IS$ requires C, 46·7; H, 4·4%. $C_{16}H_{18}N_3IS,\frac{1}{2}H_2O$ requires C, 45·7; H, 4·5%). Further crystn. failed to alter its composition (see also p. 253), even when the sample was dried only at laboratory temp. over P_2O_5; so the substance occurs normally as a hemihydrate.

Methylene-blue thiocyanate was obtained from the chloride and KCNS in lustrous needles which occurred in two forms: (1) golden-brown (Found: C, 59·0, 59·0; H, 5·35, 5·35. $C_{17}H_{18}N_4S_2$ requires C, 59·6; H, 5·25%); (2) beetle-green (Found: C, 58·95; H, 5·3%). The two forms separated from the same mother-liquor.

Methylene-blue base was prepared from the chloride by the rapid action of aq. Ag_2O at lab. temp. The deep-blue filtrate was repeatedly extracted with Et_2O and then allowed to evaporate. A dark blue cake was obtained, very sol. in H_2O or EtOH and moderately sol. in $CHCl_3$ (Found, in samples dried over P_2O_5: C, 57·8, 56·9, 56·3; H, 6·4, 6·3, 6·0; N, 12·4. $C_{16}H_{19}ON_3S,2H_2O$ requires C, 57·0; H, 6·8; N, 12·4%). When further dried in vac. at 80°, the substance approximated in composition to the anhyd. base (Found: C, 62·8; H, 5·9. $C_{16}H_{19}ON_3S$ requires C, 63·8; H, 6·3%).

Leucomethylene-blue was prepared from methylene-blue iodide and phenylhydrazine in MeOH (cf. Landauer and Weil, *Ber.*, 1910, **43**, 198). It formed pale yellow needles from light petroleum and C_6H_6 (Found: C, 67·2; H, 6·75. Calc.: C, 67·4; H, 6·7%).

Leucomethylene-blue Dihydriodide (IV).—(1) Methylene-blue iodide (1 g.) was refluxed with EtOH (50 c.c.) and EtI (30 c.c.) for 18 hr.; the colour changed to brown, and yellow crystals (1 g.) separated (Found: C, 35·4, 35·5; H, 3·9, 3·4; N, 7·4, 7·45. $C_{16}H_{21}N_3I_2S$ requires C, 35·5; H, 3·9; N, 7·75%).

(2) Powdered methylene-blue iodide (2 g.) was gradually added to alc. HI (10 c.c.) containing 0·25 g. HI per c.c. The *dihydriodide* was washed with alc. HI and then with EtOH, and dried over P_2O_5 (Found: I, 46·9. $C_{16}H_{21}N_3I_2S$ requires I, 46·9%). It can be crystallised from dil. AcOH containing HI or from $CH_3·CN$ and $CHCl_3$; m. p. 247°. It is sparingly sol. in EtOH and insol. in C_6H_6, and its aq. solutions are oxidised at once by H_2O_2, $FeCl_3$, dil. HNO_3, or I_2, becoming deep blue. NaOH, $NaHCO_3$, pyridine, or potassium metabisulphite transforms it into leucomethylene-blue.

Leucomethylene-blue Dimethiodide (III).—(1) Leucomethylene-blue (from 5 g. of methylene-blue chloride) was refluxed with MeOH (30 c.c.) and MeI (10 c.c.) for 3½ hr.; the solid product was recrystallised from EtOH and from H_2O (charcoal) and obtained as light yellow plates of the *dihydrate*, m. p. 229° (decomp.) (Found: C, 35·55, 35·7; H, 4·9, 4·8; N, 6·8; I, 42·6. $C_{18}H_{25}N_3I_2S,2H_2O$ requires C, 35·7; H, 4·8; N, 6·9; I, 42·0%). On being dried at 105° in a stream of N, it became anhyd. (Found: C, 37·65; H, 4·85. $C_{18}H_{25}N_3I_2S$ requires C, 37·95; H, 4·4%. Loss on drying: found, 6·3; calc., 6·0%).

(2) A mixture of leucomethylene-blue (7 g.), MeI (6·3 c.c.), and MeOH (9 c.c.) became warm and set to a solid mass. After 2 days, the product was crystallised from H_2O, the dimethiodide being obtained as light yellow plates. It was converted by Ac_2O at 100° into its N-*acetyl* derivative (III, with NAc in place of NH), which crystallised from H_2O as light yellow needles, m. p. 234° (decomp.) of the *dihydrate* (Found: C, 36·9; H, 4·8. $C_{20}H_{27}N_3I_2S,2H_2O$ requires C, 37·1; H, 4·8%), and formed an orange picrate. Leucomethylene-blue dimethiodide is moderately easily sol. in H_2O and in MeOH; it crystallises unchanged from aq. NaOH. The aq. solution is neutral and at once gives AgI with $AgNO_3$, and a soluble base with Ag_2O; $FeCl_3$ or H_2O_2 liberates I. It forms a picrate (orange needles from MeOH).

When the methylation of leucomethylene-blue was carried out in a sealed tube at 120° with MeI and MeOH (Bernthsen, *Annalen*, 1885, **230**, 73), much decomp. took place, and the only cryst. product isolated was not *N*-methyl-leucomethylene-blue dimethiodide (Calc.: C, 39·1; H, 4·6; N, 7·2%) as claimed by Bernthsen, but a mixture (Found: C, 36·65; H, 4·9; N, 8·1%) probably consisting chiefly of leucomethylene-blue dimethiodide.

(3) The mother-liquors from the prepn. of methylene-blue iodide monohydriodide (method 1; p. 252) contained leucomethylene-blue dimethiodide, obtained as the dihydrate after crystn. from H_2O and EtOH (Found: C, 35·45; H, 5·0%). Analyses of the crude light yellow material from the mother-liquors, however, showed that another closely similar substance was also present; this was not isolated in a pure state.

(4) Methylene-blue iodide (0·5 g.) was refluxed for 90 hr. with MeOH (20 c.c.) and MeI (15 c.c.). The brown cryst. mass (0·62 g.) was recrystallised from MeOH, giving chiefly leucomethylene-blue dimethiodide. Leucomethylene-blue dihydriodide was shown to be absent.

Methylene-blue Iodide Monohydriodide (I or II).—(1) Methylene-blue iodide (60 g.) was refluxed for 33 hr. with MeOH (2400 c.c.) and MeI (100 c.c.); more MeI (50 c.c.) was then added, and the heating continued for 7 hr. Dark purple crystals (65 g.), free from methylene-blue iodide, were obtained (yield, 83%).

The *iodide monohydriodide* formed dark purple needles from acetonitrile, in which it was moderately easily sol. It was almost insol. in cold H_2O, and decomposed on boiling; it was insol. in Et_2O or C_6H_6. It decomposed without melting if heated to 250°, but when plunged into a bath at 210° it melted and decomposed at 217°. Many samples were analysed, after being dried over P_2O_5 or in vac. at 110°; some were recrystallised from $CH_3·CN$ (Found: C, 35·5, 35·7, 35·7, 35·6, 35·9, 36·0; H, 3·4, 3·6, 3·65, 3·55, 3·45, 3·5; N, 7·5, 7·5, 8·0; I, 47·4, 47·55. $C_{16}H_{19}N_3I_2S$ requires C, 35·6; H, 3·5; N, 7·8; I, 47·1%).

(2) Methylene-blue iodide (1 g.) was dissolved in boiling EtOH (100 c.c.), the solution filtered,

EtI (10 c.c.) added, and the mixture refluxed for 1½ hr.; the iodide monohydriodide crystallised on cooling (Found : C, 35·75; H, 3·4; N, 7·45%).

(3) Leucomethylene-blue (0·197 g.) was dissolved in warm CH_3·CN (10 c.c.), and a solution of I (0·175 g.; 2 atoms) in CH_3·CN added. Immediate pptn. of a dark product (0·298 g.; yield, about 80%) occurred, and this gave the pure iodide monohydriodide after one crystn. from CH_3·CN.

(4) A fourth method is described on p. 253.

Methylene-blue Iodide Dihydriodide (V or VI).—(1) Methylene-blue iodide monohydriodide (35 g.) was boiled for 1 hr. with MeOH (1 l.), and the liquid cooled and decanted; these operations were repeated 14 times with fresh alcohol. The final extracts had only a very light blue colour. The remaining solid (16 g.) was a bronze cryst. powder, which was recrystallised from hot MeOH, in which it was only sparingly sol. It separated as magnificent copper-bronze needles or prisms, m. p. 200° (decomp.) (Found : C, 28·9, 29·1, 29·1, 29·1; H, 2·9, 3·05, 2·8, 2·9; N, 6·4. $C_{16}H_{20}N_3I_3S$ requires C, 28·8; H, 3·0; N, 6·3; I, 57·1%). Evaporation of the methyl-alc. extracts in the above prepn. left methylene-blue iodide and a little of the iodide dihydriodide. When the iodide dihydriodide was crystallised from MeOH, it frequently separated in a second form consisting of black lustrous crystals, easily transformed into the bronze form by heating to 150° or by recrystn. (Found, in black form : C, 29·1; H, 2·9%). Methylene-blue iodide dihydriodide was almost insol. in H_2O; but it was fairly readily sol. in hot CH_3·CN to a deep blue solution, from which it separated in golden-bronze or purple-red, long, thin needles containing ½CH_3·CN (Found : C, 29·8; H, 3·0; N, 6·85. $C_{16}H_{20}N_3I_3S$,½CH_3·CN requires C, 29·7; H, 3·1; N, 7·1%). On being heated at 110° over NaOH, it lost 2·5% in wt. (calc. for ½CH_3·CN, 3·0) and left the solvent-free iodide dihydriodide (Found : C, 29·1; H, 2·8; N, 6·4%). When recryst. from CH_3·CN containing AcOH, the substance again separated with solvent (Found : C, 30·0; H, 3·15%) as purple needles with golden reflex; the crystals became green when the solvent was removed by heating.

(2) When methylene-blue iodide monohydriodide (2·18 g.) was extracted with boiling H_2O (5 × 100 c.c.), there remained a dull-green powder (1·24 g.) of the crude iodide dihydriodide; the aq. extracts, filtered, and concentrated, gave methylene-blue iodide (0·77 g.), so the yields of the two products were over 90%. The iodide dihydriodide prepared by this method was difficult to purify; it crystallised from CH_3·CN in flat, black, lustrous needles, m. p. 190° (decomp.), which became purple when dried over P_2O_5 (Found : C, 29·8, 29·95; H, 2·9, 2·9%); and when further dried in vac. at 110° (loss, 2·5, 2·9%) became green (Found : C, 29·5, 29·4; H, 2·9, 2·9%). Careful purification, by means of hot MeOH and then H_2O, separated the dull-green powder (0·543 g.) into the characteristic bronze crystals (0·46 g.) and methylene-blue iodide (0·048 g.), together with traces of a whitish substance.

(3) The direct addition of HI to methylene-blue iodide in AcOH gave rise to the iodide dihydriodide, whether 1 or 2 mols. of HI were employed :

(*a*) Methylene-blue iodide (0·5 g.) in hot AcOH (500 c.c.) was treated with 0·156 g. (1 mol.) of HI in AcOH. Blackish crystals (0·369 g., m. p. 191°) were pptd.; when cryst. from CH_3·CN and then from CH_3·OH, this material gave the bronzed form of the iodide dihydriodide. The material cryst. from CH_3·CN lost 3·4% of its wt. on drying at 110° (Found in dried material : C, 29·2; H, 2·8%). The AcOH mother-liquor was deep blue.

(*b*) When 2 mols. HI were used in the above prepn., the product (0·457 g.) was again the iodide dihydriodide [Found in dried material (loss, 2·7%) : C, 29·2; H, 2·75%]; the AcOH mother-liquor was then only light green and contained a leuco-compound.

It is evident from these expts. that 1 mol. HI ppts. half the methylene-blue iodide as its dihydriodide (yield, 90%), leaving the remainder unchanged; whereas 2 mols. HI give the same substance but at the same time occasion reduction of a portion of the methylene-blue iodide.

(4) Although in (3) the formation of methylene-blue iodide monohydriodide was not detected, yet the addition of HI (1 mol.) to that substance in AcOH gave rise to the iodide dihydriodide.

The monohydriodide (0·25 g.) was heated with AcOH (300 c.c.), and HI (1 mol.; 0·119 g.) in AcOH added. The crude iodide dihydriodide (0·237 g., or 77%) crystallised on cooling; it separated from CH_3·CN in purple-black needles which on being dried at 110° in vac. lost 3·05% in wt. and became green (Found : C, 29·1; H, 2·85%).

The iodide dihydriodide would not take up a further mol. of HI in AcOH; the dihydriodide was recovered unchanged after crystn. of the product from CH_3·CN and drying at 110° (Found : C, 29·1; H, 3·05%).

The iodide dihydriodide was converted into methylene-blue iodide, (*a*) by grinding with a solution of $K_2S_2O_5$ and extracting the residual solid with hot H_2O; (*b*) by refluxing it for several days with 100 parts of H_2O and repeating the process on the residue until all became sol.; a yield of 80% of methylene-blue iodide was thus obtained; HI was shown to be present in the filtrates.

Interaction of Methylene-blue Iodide and its Dihydriodide.—Equimolecular proportions of these two substances (0·100 g. and 0·162 g. respectively) were dissolved in $CH_3{\cdot}CN$ (45 c.c.), and the mixture refluxed for 1 hr. The liquid was filtered, and the filtrate concentrated to half bulk: dark purple-black crystals of methylene-blue iodide monohydriodide (0·187 g.) separated (Found: C, 35·95; H, 3·4%).

Interaction of Methylene-blue Iodide Dihydriodide with Quinoline.—The iodide dihydriodide (0·530 g.) was heated on the water-bath with quinoline (20 c.c.) for 1½ hrs. Complete solution occurred and then crystals of methylene-blue iodide (0·314 g.; 83%) separated from the hot solution in combination with ½ mol. quinoline (Found: C, 50·9; H, 4·8. Calc.: C, 51·7; H, 4·5%). The methylene-blue iodide was recrystallised once from H_2O and obtained pure ($+\frac{1}{2}H_2O$) (Found: C, 45·9; H, 4·95. Calc.: C, 45·7; H, 4·5%). The quinoline solution, which was blue, was repeatedly extracted with H_2O (800 c.c.) until no more halogen was present in the extracts. Colorimetric comparison showed that the aq. extract contained not more than 0·004 g. of methylene-blue iodide; whilst estimation with HNO_3 and $AgNO_3$ gave 0·302 g. AgI, corresponding to 31% HI present in the iodide dihydriodide (calc., 38·4% HI).

In another expt., the quinoline hydriodide (Found: I, 49·2%. Calc.: 49·4%) was isolated and compared with an authentic specimen made from quinoline and HI. Both samples formed lemon-yellow prisms from EtOH; m. p. 145—146° (Trowbridge, *J. Amer. Chem. Soc.*, 1899, **21**, 66, gives m. p. 135°); the hydriodide is very sol. in H_2O (solution neutral to Congo-red; acid to litmus), sparingly sol. in C_6H_6, and almost insol. in Et_2O.

It was shown in a separate expt. that methylene-blue iodide liberates only minute traces of halogen when treated with quinoline and H_2O as above.

Estimations with Titanous Chloride.—Although methylene-blue iodide and Bindschedler's-green iodide monohydriodide gave reproducible and satisfactorily accurate estimations of the H (2 atoms per mol.) required for their reduction to the leuco-compounds, when their alc. solutions were titrated with $TiCl_3$($N/20$ or $N/60$) under the usual conditions, yet both hydriodides of methylene-blue iodide were found, probably on account of their low solubility, to be unsuitable for this method of analysis. As the average of a number of expts., about 2·4 atoms of H appeared to be absorbed during the reduction of 1 mol. of either of the latter substances, but the results were not accurately reproducible owing to extraneous oxidation of the $TiCl_3$ during the somewhat prolonged periods necessary for the interactions.

Bindschedler's-green was obtained by the oxidation of dimethylaniline and *p*-aminodimethylaniline (Wieland, *Ber.*, 1915, **48**, 1078) and was purified as the zincichloride. Bindschedler's-green iodide was prepared from this, by means of KI (Nietzki, *Ber.*, 1883, **16**, 464), in thin green needles.

Leuco-Bindschedler's-green was prepared from the zincichloride by means of sodium hydrosulphite (Wieland, *loc. cit.*); colourless plates, m. p. 121°, from light petroleum or aq. EtOH.

Bindschedler's-green Iodide Monohydriodide.—(1) A solution of the leuco-compound (0·541 g.) in $CH_3{\cdot}OH$ (15 c.c.) was treated with I (0·541 g.; 1 mol.) in $CH_3{\cdot}OH$ (10 c.c.). Small dark needles (1·025 g.) separated, forming blue-black prisms, m. p. 152—153° (decomp.), from EtOH (Found: I, 50·4. $C_{16}H_{21}N_3I_2$ requires I, 49·9%).

(2) Bindschedler's-green iodide (0·5 g.) was refluxed with MeOH (10 c.c.) and MeI (1 c.c.) for 1 hr.; on cooling, the iodide monohydriodide (0·3 g.) crystallised.

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