886. *Tetrahydro- and Octahydro-4,7-phenanthroline and Octahydro-1,5-diaza-anthracene.*

By W. O. Sykes.

The direct reduction of 4,7-phenanthroline is re-examined and new preparations of the tetrahydro- and octahydro-derivative are described; confirmatory evidence is presented for the structure of the tetrahydrophenanthroline. Smith and Tung-Yin Yu's octahydro-base [1] is shown to be octahydro-1,5-diaza-anthracene and not, as claimed, its angular isomer, octahydrophenanthroline.

MATSUMURA [2] described the preparation of tetrahydrophenanthroline (I) by reducing 4,7-phenanthroline with sodium and pentanol (unspecified isomer) or with tin and hydrochloric acid; Wibaut, Spiers, and Ouweltjes [3] repeated the latter preparation and identified as tetrahydrophenanthroline a by-product of the Skraup synthesis applied to *p*-phenylenediamine. On the other hand, after using for the reduction larger proportions of tin and acid than those specified by Matsumura,[2] Ochiai and Kuroyanagi [4] detected octahydrophenanthroline (II) in the product although, apparently, it was still in smaller proportion than would conflict with the yield of tetrahydrophenanthroline claimed for Matsumura's [2] preparation. We have established that the tetrahydro- and the octahydro-base are present together in the tin and acid reduction product, with tetrahydrophenanthroline predominating in the fraction analysed, but we have found octahydrophenanthroline to be the principal product of reduction by sodium and pentanol. No essential difference

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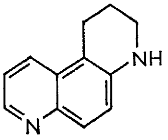
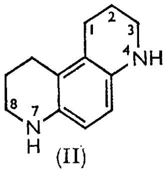
[1] Smith and Tung-Yin Yu, *J. Amer. Chem. Soc.*, 1952, **74**, 1096.
[2] Matsumura, *J. Amer. Chem. Soc.*, 1935, **57**, 495.
[3] Wibaut, Spiers, and Ouweltjes, *Rec. Trav. chim.*, 1937, **56**, 1219.
[4] Ochiai and Kuroyanagi, *J. Pharm. Soc. Japan*, 1943, **63**, 213.

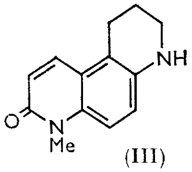
was found between the products when the latter reduction was carried out in pentan-1-ol or in crude isopentyl alcohol, and it is unlikely, therefore, that the discrepancy between our findings and Matsumura's [2] arises from differences in composition of the alcohols used.



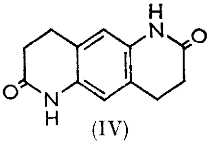
(I)



(II)



(III)



(IV)

By hydrogenation of phenanthroline in the presence of Raney nickel, Searles and Warren [5] obtained tetrahydrophenanthroline together with 5,6-dihydro-4,7-phenanthroline, but Ochiai and Kuroyanagi,[4] working with very much higher pressures and temperatures, prepared octahydrophenanthroline and the fully saturated compound. There is a large difference between the melting range quoted by Ochiai and Kuroyanagi [4] for their octahydrophenanthroline (130—140°) and that found by us for the above sodium–pentanol reduction product (110—111° with previous softening), but both these unstable octahydro-bases yield a readily purified diacetyl derivative identical with the one obtained from the tin and acid reduction product; when our base was recovered from its purified diacetyl derivative it had no higher melting point than before. The formation of diacyl derivatives and a dinitroso-derivative from octahydrophenanthroline supports its formulation as (II).

We have now found that finely divided platinum catalyses the hydrogenation of phenanthroline at near-atmospheric pressure. About two mol. of hydrogen were taken up, but the product was a mixture from which only tetrahydrophenanthroline was isolated, in moderate yield. The structure (I) has hitherto been attributed to tetrahydrophenanthroline on the strong but essentially negative evidence that only monoacyl derivatives can be prepared,[2,3] and this evidence has now been re-inforced by the following finding: Acetyltetrahydrophenanthroline formed a methiodide which was oxidised to the corresponding dihydro-*N*-methyl-oxo-compound, and the acetyl group was then removed by acid-hydrolysis; the resulting base was identical with the compound (III) obtained in good yield by catalytic hydrogenation of 3,4-dihydro-4-methyl-3-oxo-4,7-phenanthroline.

Reduction of the supposed [6] 1,2,3,4,7,8,9,10-octahydro-3,8-dioxo-4,7-phenanthroline (*A*) by aluminium lithium hydride produces [1] an octahydro-base which is not the same as our octahydrophenanthroline although the two bases yield the same tetradecahydrodiazaperylene when refluxed with 3-bromopropyl chloride. If the possibility of stereoisomerism in octahydrophenanthroline is discounted, the two octahydro-bases must be linear and angular isomers, and the dioxo-compound (*A*) must, in fact, be the known [7] 1,2,3,4,5,6,7,8-octahydro-2,6-dioxo-1,5-diaza-anthracene (IV). It is interesting that this compound is prepared by double cyclisation with aluminium chloride of *NN'*-di-β-chloropropionyl-*p*-phenylenediamine, and that from the similar cyclisation of *NNN'N'*-tetrakis-2'-cyanoethyl-*p*-phenylenediamine Braunholz and Mann [8] did obtain, although only in one of their preparations, the linear isomer instead of their usual 4,7-phenanthroline derivative. Identification of product (*A*) by direct comparison with the authentic material (IV) is not practicable since neither compound melts within the ordinarily determined limits [6,7] and both eventually sublime when heated on a hot-plate. Degradations with boiling aqueous permanganate of the dioxo-compound (*A*) and the corresponding acetylated octahydro-base both failed to provide any recognised derivative of the sought product, 2,5-diaminoterephthalic acid, although in the latter case the finding of a diazotisable amine in an acid-hydrolysed sample of the reaction solution suggested that the degradation

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[5] Searles and Warren, *J. Org. Chem.*, 1953, **18**, 1317.
[6] Mayer, van Zütphen, and Philipps, *Ber.*, 1927, **60**, 858.
[7] Ruggli and Preiswerk, *Helv. Chim. Acta*, 1939, **22**, 478.
[8] Braunholz and Mann, *J.*, 1953, 1817.

had followed the desired course. However, Smith and Tung-Yin Yu's [1] octahydro-base, from (*A*), was also obtained by reduction of the authentic base (IV) and, therefore, (*A*) is the same compound as (IV), and the derived base must be octahydrodiaza-anthracene.

This finding also verifies what was assumed to be true for one step in Ruggli and Preiswerk's [7] synthesis of the dioxo-compound (IV) from terephthaldialdehyde namely, that 7-2′-carboxyethyl-3,4-dihydrocarbostyril is nitrated first in position 6. Evidence against the alternative 8-nitration was to be found in the non-identity of the dioxo-compound and of the derived parent base [7] with their 1,10-phenanthroline isomers.

EXPERIMENTAL

1,2,3,4-*Tetrahydro*-4,7-*phenanthroline* (I).—Glacial acetic acid (100 c.c.) was added to 4,7-phenanthroline (10 g.) dissolved in hot absolute ethanol (100 c.c.), and the mixture was cooled so as to produce fine crystals. It was shaken with platinic oxide (1 g.) and hydrogen at slightly above atmospheric pressure; absorption of hydrogen almost ceased after 6 hr. when nearly 2 mol. had been taken up. The resulting dark brown solution was filtered, the ethanol was largely removed, and the residue was diluted with dilute hydrochloric acid and then basified with ammonia solution to precipitate a dark, slowly solidifying oil; this was dried in a desiccator and extracted with several portions of boiling benzene, leaving a black tar. The extracted material was distilled under reduced pressure to separate a solidifying distillate (4 g.; b. p. up to about 235°/15 mm.) from a residue, of much higher b. p., which decomposed on strong heating. The distillate was tetrahydrophenanthroline, m. p. about 147°, which crystallised from acetone as yellow prismatic needles, m. p. 150—151°, b. p. 222°/12 mm. (recorded m.p. 152—152·5°,[2] 152°,[3] 152·5—154°,[5] b. p. 212—213°/12 mm.[2]) (Found: C, 77·6; H, 6·5. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6%). The acetyl derivative, prepared by refluxing the amine with acetic anhydride alone, formed prisms (from benzene–light petroleum), m. p. 120° (recorded m. p. 121°,[3] 120—120·5° [5]). The benzoyl derivative, obtained by heating the amine briefly with an excess of benzoic anhydride, decomposing the cooled mixture with concentrated aqueous ammonia, and then washing the solid product with hot water, formed prisms (from alcohol), m. p. 179° (recorded m. p. 183·5°,[2] 180·7—181·0° [3]). The *nitroso-derivative* crystallised in pale yellow needles (from benzene–light petroleum), m. p. 154° (Found: C, 68·4; H, 5·3. $C_{12}H_{11}N_3O$ requires C, 67·6; H, 5·2%).

The residue left from crystallisation of the distilled tetrahydrophenanthroline, when taken into dilute mineral acid solution and treated with sodium nitrite solution, yielded directly a brown precipitate (very variable amount; ~0·1 g.) which must have contained the nitroso-derivative of any octahydrophenanthroline present: it was not further examined.

1,2,3,4,7,8-*Hexahydro*-7-*methyl*-8-*oxo*-4,7-*phenanthroline* (III).—(*a*) 3,4-Dihydro-4-methyl-3-oxo-4,7-phenanthroline [9] (5 g.) in glacial acetic acid (75 c.c.) was shaken with platinic oxide (0·5 g.) under hydrogen at slightly above atmospheric pressure (absorption, nearly 2 mol. in about 3 hr.) The deep yellow solution was filtered and evaporated *in vacuo* and the residue was dissolved in dilute hydrochloric acid (charcoal) and reprecipitated with ammonia solution. The *hexahydro-compound* (III) (4 g.) thus produced crystallised from chlorobenzene as yellow needles, m. p. 218—219° (Found: C, 72·8; H, 6·7. $C_{13}H_{14}N_2O$ requires C, 72·9; H, 6·6%).

(*b*) Acetyltetrahydrophenanthroline (1 g.) was heated in a sealed tube with methyl iodide (2 g.) and methanol (2 c.c.) at 100° for 15 min. The solid methiodide (1·4 g.) was separated from the cooled mixture and crystallised from methanol as yellow leaflets, m. p. 235° with previous darkening and softening. It (1 g.) was oxidised with potassium ferricyanide in alkaline solution, and the product, which was precipitated when the solution was further basified, was hydrolysed by refluxing 20% w/v hydrochloric acid (5 c.c.) for 30 min. The base (III) (0·4 g.) was precipitated from the diluted solution (charcoal) with ammonia solution and crystallised from chlorobenzene as yellow needles, m. p. and mixed m. p. 218—219°.

The *acetyl derivative*, formed either by refluxing the base in acetic anhydride solution or by oxidising the appropriate methiodide [(*b*), above], crystallised from ethyl acetate as colourless needles, m. p. 173° (Found: C, 70·1; H, 6·3. $C_{15}H_{16}N_2O_2$ requires C, 70·3; H, 6·3%). The *nitroso-derivative*, precipitated on mixing a solution of the base in dilute mineral acid with

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[9] Kaufmann and Radošević, *Ber.*, 1909, **42**, 2612; Douglas, Jacomb, and Kermack, *J.*, **1947**, 1659.

sodium nitrite solution, crystallised from benzene–light petroleum as pale yellow needles, m. p. (decomp.) about 210° (Found: C, 63·7; H, 5·4. $C_{13}H_{13}N_3O_2$ requires C, 64·2; H, 5·4%).

1,2,3,4,7,8,9,10-*Octahydro*-4,7-*phenanthroline* (II).—4,7-Phenanthroline (5 g.) was reduced with sodium and pentan-1-ol essentially as described by Matsumura.[2] The total base extracted by dilute hydrochloric acid from the water-washed pentanol solution was precipitated with aqueous sodium hydroxide and taken up into benzene. Evaporation of the dried (Na_2SO_4) benzene solution to about 15 c.c. gave a first crop of brown octahydrophenanthroline (2½ g.; m. p. about 109°) which by recrystallisation from benzene formed almost colourless needles, m. p. 110—111° after softening (Found: C, 77·5; H, 8·5. Calc. for $C_{12}H_{16}N_2$: C, 76·6; H, 8·6%); Ochiai and Kuroyanagi [4] described their octahydrophenanthroline as being brown, of m. p. 130—140° (no analysis). The compound resinified when heated below its m. p., and gradually darkened on exposure, an instability similar to that described by Ochiai and Kuroyanagi [4] for their product. The pure base boiled at b. p. 214°/14 mm. without obvious decomposition, but the m. p. of the distillate was low. Distillation proved useful, however, for the preliminary purification of the otherwise intractable residue from the first crystallisation of octahydrophenanthroline; the syrupy distillate from combined residues yielded the base (a further ½—1 g.) by crystallisation from benzene.

The diacetyl derivative, formed by refluxing the base with acetic anhydride, crystallised from ethyl acetate as colourless needles, m. p. 181—182° (Ochiai and Kuroyanagi [4] give m. p. 181°) (Found: C, 70·2; H, 7·3. Calc. for $C_{16}H_{20}N_2O_2$: C, 70·6; H, 7·4%). The dibenzoyl derivative, formed by briefly heating the base with benzoic anhydride, crystallised from methanol as colourless prisms, m. p. 190—191° (Ochiai and Kuroyanagi [4] give m. p. 189—191°). The *dinitroso-derivative*, prepared as above, crystallised from benzene as needles, m. p. 163° (decomp.) (Found: C, 58·6; H, 5·7. $C_{12}H_{14}N_4O_2$ requires C, 58·5; H, 5·7%). The compound discolours in hot solutions.

No considerable proportion of tetrahydrophenanthroline was detected in the reduction product, but a small amount (~0·1 g. per 5 g.) was obtained by crystallising, from acetone, the oily residue left after the final recovery of octahydrophenanthroline by vacuum-distillation and crystallisation.

Reduction of 4,7-*Phenanthroline by Tin and Acid.*—Phenanthroline (5·4 g.) was refluxed with granulated tin and concentrated hydrochloric acid as described by Matsumura [2] and the reaction mixture was poured, with stirring, into a hot 40% w/v solution of sodium hydroxide (300 c.c.). The precipitate of mixed bases together with some tin oxide was separated, drained at the pump, powdered with anhydrous potassium carbonate, and extracted with several portions of boiling benzene. The syrupy residue recovered from the combined benzene extracts was distilled under reduced pressure, yielding a fraction, b. p. up to ~235°/15 mm., and a residue of much higher-boiling material. The orange distillate (3 g.) crystallised from a small volume of acetone to yield crude tetrahydrophenanthroline (1·3 g.), m. p. ~145° improved to 150° by one crystallisation from acetone; the once-crystallised tetrahydrophenanthroline contained very little of the octahydro-compound as judged by the production of no more than a faint turbidity on treatment with sodium nitrite. The residue from the evaporated acetone mother-liquors was acetylated, to yield a very impure product from which was obtained, by extraction with ethyl acetate, diacetyloctahydrophenanthroline (½—1 g.), m. p. ~178° improved by recrystallisation from ethyl acetate to 181—182° and not depressed on admixture with the product described above.

1,2,3,4,5,6,7,8-*Octahydro*-1,5-*diaza-anthracene*.—The 2,6-dioxo-compound, colourless leaflets from glacial acetic acid, not melting below 300° (Found: C, 67·0; H, 5·7. Calc. for $C_{12}H_{12}N_2O_2$: C, 66·7; H, 5·6%), described by Mayer, van Zütphen, and Phillips [6] as the isomeric phenanthroline derivative, was reduced (2 g.) with lithium aluminium hydride essentially as described by Smith and Tung-Yin Yu.[1] The product, *octahydrodiaza-anthracene* (crude yield 1 g.) crystallised as almost colourless plates, m. p. 161—162°, from ethyl acetate or benzene (Smith and Tung-Yin Yu [1] give m. p. 161—162°) (Found: C, 77·1; H, 8·5; N, 14·7. $C_{12}H_{16}N_2$ requires C, 76·6; H, 8·6; N, 14·9%). This compound, unlike octahydrophenanthroline, is fairly stable to exposure or heating but, like octahydrophenanthroline, gives an intense red colour when treated in acetone with aqueous hydrogen peroxide. The same compound (m. p. and mixed m. p. 161—162°) (crude yield 0·1 g.) was obtained by the same method from Ruggli and Preiswerk's [7] dioxo-compound (0·2 g.).

The *diacetyl derivative*, formed by refluxing the base in acetic anhydride, crystallised from ethyl acetate as colourless prismatic needles, m. p. 195—196° (Found: C, 71·1; H, 7·3%). Like diacetyloctahydrophenanthroline, this derivative showed white fluorescence in ultraviolet light, followed by yellow phosphorescence.

1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-*Tetradecahydro*-3a,9a-*diazaperylene*.—Octahydrophenanthroline (0·5 g.) was condensed with 3-bromopropyl chloride by the method applied by Smith and Tung-Yin Yu [1] to octahydrodiaza-anthracene; the crude ether solution yielded the tetradecahydrodiazaperylene (0·2 g.), m. p. (from ether) 189—190° with previous darkening and softening, not depressed on admixture with the product, m. p. 189—190° similarly obtained from the above octahydrodiaza-anthracene (Smith and Tung-Yin Yu [1] give m. p. 190—191°).

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