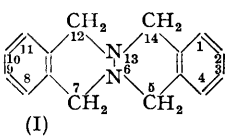
40. *Heterocyclic Nitrogen Compounds. Part II.* The Preparation of 5 : 7 : 12 : 14-Tetrahydro-6 : 13-diazanaphthacene and Some Derivatives thereof, with an Example of Ring Expansion and Contraction in a Clemmensen Reduction.*

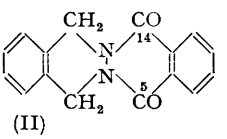
By H. H. Hatt and (Miss) E. F. M. Stephenson.

Condensation of tetrahydrophthalazine hydrochloride with ωω′-dibromo-*o*-xylene (*o*-xylylene dibromide) gives 5 : 7 : 12 : 14-tetrahydro-6 : 13-diazanaphthacene (I),* and with *o*-bromomethylbenzoyl bromide gives the 5-keto-derivative of (I). Clemmensen reduction of the 5 : 14-diketo-compound (II) proceeds with molecular rearrangement and formation, first, of the tetracyclo-compound (III) containing a 7–5-ring system. Continued reduction leads by hydrogenolysis of the 7-membered ring to the primary amine (IV), the structure of which is established by conversion into *N*-*o*-xylylphthalimidine. The mechanism of the Clemmensen reduction is discussed.

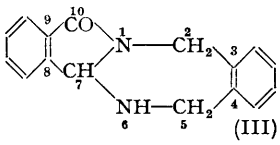
In continuation of the investigation of diazanaphthacene derivatives reported in Part I,* the parent 5 : 7 : 12 : 14-tetrahydro-6 : 13-diazanaphthacene (I) has been prepared by heating together tetrahydrophthalazine hydrochloride and ωω′-dibromo-*o*-xylene (*o*-xylylene dibromide). The 5-keto-derivative of (I) has been prepared similarly from tetrahydrophthalazine hydrochloride and *o*-bromomethylbenzoyl bromide.



(I)

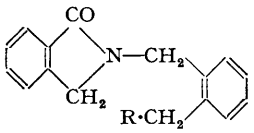


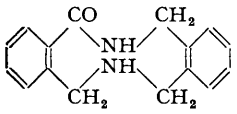
(II)



(III)

(IV; R = NH_2)
(V; R = OH)
(VI; R = Cl)
(VII; R = H)





(VIII)

The tetrahydrodiazanaphthacene (I) is basic and forms well-defined salts, in contrast to the related tetrabenzylhydrazine (Wieland and Schamberg, *Ber.*, 1920, **53**, 1329). Its stability also is noteworthy : it is unaffected by most hydrolytic and reducing agents, for instance, zinc and concentrated hydrochloric acid, under conditions which suffice to sever the nitrogen–nitrogen bond of phthalazine.

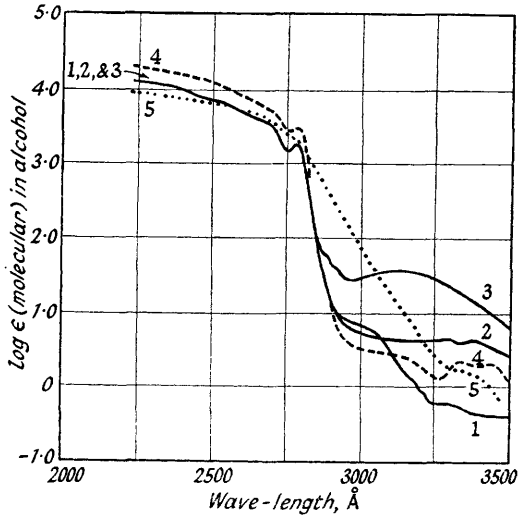
The above syntheses are not very convenient, since tetrahydrophthalazine is not readily prepared. Reduction of the more accessible 5 : 14-diketo-compound (II) (Part I) could provide a more convenient method, but (II) is resistant to most reducing agents, and the Clemmensen reagent, which does reduce it, severs the nitrogen–nitrogen bond. Catalytic methods of reduction have yet to be examined. The chief products of the Clemmensen reduction of (II) were two compounds which have been assigned structures (III) and (IV). In addition, some ωω′-diamino-*o*-xylene was always formed, although usually in small quantity. If the amount of hydrochloric acid used was restricted, or if the reaction time was short, 10-keto-1 : 6-diaza-3 : 4-8 : 9-dibenzo*bicyclo*[5 : 3 : 0]deca-3 : 8-diene (III) was the major product; otherwise (IV) predominated, and with long reaction times (III) disappeared, being reduced to (IV) although not quantitatively.

Compound (III) is monoacidic, forms monoacyl and mononitroso-derivatives, and can be recovered from the last by hydrolysis. Concentrated hydrochloric acid hydrolyses (III) to ωω′-diamino-*o*-xylene and phthalaldehydic acid (isolated as 3-ethoxyphthalide).

* Part I, *J.*, 1943, 658, where (I) was named on the Ring Index system (*i.e.*, as a tetrahydro-derivative of diazanaphthacene rather than as a diaza-derivative of hexahydronaphthacene) but numbered on an arbitrary system. In the present paper, the Ring Index names are retained but the numbering is changed to that required by the Ring Index system.

These facts establish its structure and explain the failure to reduce it quantitatively to (IV). The infra-red spectrum also agrees with structure (III). Absorption bands appear at 1624 cm.$^{-1}$ (NH deformation), 1683 cm.$^{-1}$ (C=O stretching), and 3280 cm.$^{-1}$ (NH stretching). The 1624 cm.$^{-1}$ band could be ascribed to C=N stretching, but occurs also in the spectrum of phthalimidine, which shows no OH band and can therefore show no bands attributable to C=N.

N-o-Aminomethylbenzylphthalimidine (IV) forms a monohydrochloride, but, unlike (III), is otherwise unaffected by hydrochloric acid or by the Clemmensen reagent. Its structure follows from its conversion by nitrous acid into the corresponding primary alcohol (V), thence with hydrochloric acid into the chloromethyl compound (VI), and finally by reduction of this with zinc and acetic acid into *N-o*-xylylphthalimidine (VII), identical with the reduction product of *N-o*-xylylphthalimide. In agreement with structure (IV), the product from the Clemmensen reduction forms mono-benzoyl, -toluene-*p*-sulphonyl, and -2 : 4-dinitrophenyl derivatives, and gives a benzylidene derivative under acid catalysis. A comparison of the ultra-violet absorption spectra of (III), (IV), (V), (VII), and *N*-benzylphthalimidine also gives support to structure (IV) (see figure). The absorption spectrum



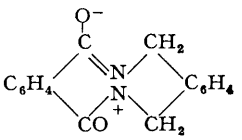
(1) N-o-*Xylylphthalimidine.*
(2) N-o-*Aminomethylbenzylphthalimidine.*
(3) N-o-*Hydroxymethylbenzylphthalimidine.*
(4) N-*Benzylphthalimidine.*
(5) 10-*Keto*-1 : 6-*diaza*-3 : 4-8 : 9-*dibenzo*-bicyclo[5 : 3 : 0]*deca*-3 : 8-*diene.*

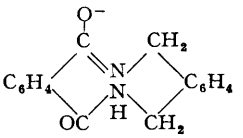
of (III) differs noticeably from the others, which strongly resemble one another. These last all exhibit a characteristic small band at 2780 Å, which for *N*-benzylphthalimidine has a molecular extinction coefficient of 2650. The other three compounds, (IV), (V), and (VII), possess almost identical molecular extinction coefficients at this wave-length : 1560, 1590, and 1550, respectively, agreeing with their similar structures. The infra-red spectrum of (IV) in a Nujol suspension shows absorption bands at 1622 cm.$^{-1}$ (NH deformation), weak 1639 cm.$^{-1}$ (C=N stretching?), 1683 cm.$^{-1}$ (C=O stretching), and at 3295 and 3370 cm.$^{-1}$ (NH stretching).

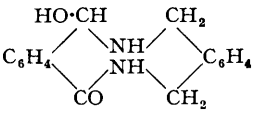
Some difficulties, however, arise in accepting formula (IV) as the sole structure. The arylsulphonyl derivatives are insoluble in alkali, and the compound is unstable to alcoholic sodium ethoxide towards which (V) and other *N*-substituted phthalimidines are stable. The compound also gives a diacetyl derivative of unexpected stability, for although it can be hydrolysed again to the parent base, it has not yet been hydrolysed to a monoacetyl derivative. These properties may mean that (IV) can undergo some isomerisation to the ten-ring structure (VIII).

The reduction of (II) to (III) is an example of a molecular rearrangement during the course of a Clemmensen reduction which involves ring expansion and contraction. It resembles the rearrangements studied by Prelog, Clemo, Leonard, and their respective co-workers (Prelog and Seiwerth, *Ber.*, 1939, **72**, 1638; Clemo, Raper, and Vipond, *J.*, 1949, 2095; Clemo and Vipond, *Chem. and Ind.*, 1949, 856; Leonard and Wildman, *J. Amer.*

Chem. Soc., 1949, **71**, 3089; Leonard and Ruyle, *ibid.*, p. 3094). It differs from them in that a nitrogen–nitrogen, not a carbon–nitrogen bond, unites positions 2 and 3 relative to the carbonyl group, and suffers fission during reduction. In this type of reduction we consider the first step to be an attack by electrons from the metal on the canonical form (IX), leading to (X) by subsequent addition of a proton, and thence to the amino-alcohol (XI) from which (III) arises by cyclisation.


(IX)


(X)


(XI)

Comparison with the behaviour of (I) shows that the carbonyl group in (II) clearly promotes hydrogenolysis of the 2 : 3-bond. In a similar manner it can be regarded as promoting hydrogenolysis of the carbon–nitrogen bond in (III), so that, although (III) is readily hydrolysed by acid to phthalaldehydic acid and ωω′-diamino-*o*-xylene, yet it can be reduced to (IV) in good yield by the Clemmensen reagent. On this explanation (III) should first be reduced to (VIII) and pass to (IV) by isomerisation.

Experimental

M.p.s are corrected. Micro-analyses were by Mr. H. L. Oates, Miss E. E. Rutherford, and by the authors.

5 : 7 : 12 : 14-*Tetrahydro*-6 : 13-*diazanaphthacene* (I).—Equimolecular quantities of dry, finely powdered 1 : 2 : 3 : 4-tetrahydrophthalazine hydrochloride (6·45 g.) and ωω′-dibromo-*o*-xylene (10 g.) were heated for 1 hour at 140—150° in the absence of moisture. After cooling, the product was ground with a little alcohol to remove tarry impurities, and the crystalline mixture of the hydrochloride and hydrobromide of the base (6·5 g.) was converted into the free base by excess of 5% aqueous sodium hydroxide. From 40% aqueous alcohol (charcoal), the free *base* crystallised in thin colourless plates, m. p. 132—133° (3·6 g.) (Found : C, 81·5 ; H, 6·6 ; N, 11·8. $C_{16}H_{16}N_2$ requires C, 81·3 ; H, 6·8 ; N, 11·9%). Gradual addition of the tetrahydrophthalazine hydrochloride to the molten dibromide did not improve this yield. Condensation did not take place in pyridine ; in boiling xylene condensation occurred, but the yield was poor. The *hydrochloride* was obtained as colourless needles (from absolute alcohol–light petroleum), m. p. 248—250° (decomp.) (Found : C, 70·5 ; H, 6·2 ; N, 10·7 ; Cl, 13·1. $C_{16}H_{17}N_2Cl$ requires C, 70·5 ; H, 6·3 ; N, 10·3 ; Cl, 13·0%). The *methiodide* separated as pale yellow parallelepipeds on addition of excess of methyl iodide to the base ; it had m. p. 221—223° (decomp.), dependent on the rate of heating (Found : I, 33·8. $C_{17}H_{19}N_2I$ requires I, 33·6%).

The base could be neither acetylated nor benzoylated. It was unaffected by alcoholic sodium ethoxide, sodium dithionite (hydrosulphite), fuming hydriodic acid, stannous chloride with alcoholic hydrogen chloride, or zinc and hydrochloric acid. It gave a colourless solution in concentrated sulphuric acid. Nitrous acid caused decomposition to unidentified products.

Oxidation of the base with potassium permanganate in acetone produced only small amounts of phthalazine, probably because under the conditions needed to attack (I) it also was attacked. From 1·0 g. of (I), 0·06 g. of phthalazine was obtained, m. p. 143·5—144·5° (identified by conversion into the methiodide and picrate and by mixed m. p.). Phthalic acid was the only other product identified.

5 : 7 : 12 : 14-*Tetrahydro*-5-*keto*-6 : 13-*diazanaphthacene*.—Finely powdered, dry tetrahydrophthalazine hydrochloride (3·0 g.) and *o*-bromomethylbenzoyl bromide (5·4 g.) were mixed and heated at 150—160°, with exclusion of moisture. After the vigorous frothing and evolution of gas had ceased (30 minutes) the temperature was increased to 200—210° and heating continued (30 minutes). The red resinous product, when cool, was triturated with a little methanol, the crystalline material was washed with a little methanol, and basic materials were removed by digestion with warm dilute hydrochloric acid. The insoluble *ketone* was dissolved in benzene, freed from coloured impurities by chromatography on alumina, and recovered from the benzene eluate. It crystallised from methanol in colourless crystals, m. p. 198—199° (decomp.) (0·7 g.) (Found : C, 76·8 ; H, 5·5 ; N, 11·3. $C_{16}H_{14}ON_2$ requires C, 76·8 ; H, 5·6 ; N, 11·2%).

Clemmensen Reduction of 5 : 7 : 12 : 14-*Tetrahydro*-5 : 14-*diketo*-6 : 13-*diazanaphthacene* (II).—The small solubility of (II) made it necessary to use alcohol as a solvent. The amounts of compounds (III) and (IV) produced from (II) depended on the amount of hydrochloric acid used, its rate of addition, and the time of reaction. From (II) with 5 parts of zinc and 20 parts of hydrochloric acid a 20—25% yield of (III) was obtained in a reaction time of 20 hours. With twice this amount of hydrochloric acid and a reaction time of 30 hours, (IV) was the main product (yield, 55—60%) and (III) was either absent or present in small amount. However, it was difficult to duplicate yields closely. In the example given below, compound (IV) is the the major product.

Amalgamated zinc (70 g.), prepared from pure zinc (B.D.H. arsenic-free), ethanol (200 ml.), concentrated hydrochloric acid (100 ml.), and 5 : 7 : 12 : 14-tetrahydro-5 : 14-diketo-6 : 13-diazanaphthacene (13·2 g., 0·05 mole) were refluxed together for 30 hours. Additional hydrochloric acid was added at 3-hourly intervals (total, 120 ml.). After the unchanged zinc had been removed, the liquors were concentrated to half bulk, a further 40 ml. of concentrated acid was added, and after 24 hours the crystalline zincichlorides were collected (A). The filtrates were made strongly alkaline with 30% aqueous sodium hydroxide and cooled, and the precipitated bases were collected by centrifuging after 24 hours (B). The aqueous layers were usually discarded, but ωω′-diamino-*o*-xylene could be slowly distilled from them in steam and was isolated as the hydrochloride (m. p. 310°, decomp.) and identified by conversion into the dibenzoyl derivative (m. p. and mixed m. p. 189—190°). Gabriel and Pinkus (*Ber.*, 1893, **26**, 2213) reported m. p. 184°.

The zincichlorides (A) were decomposed by dissolving them in 250 ml. of 50% aqueous acetic acid, liberating the bases as oils with excess of 30% aqueous sodium hydroxide, and collecting them when solidified. From this material and (B), compounds (III) and (IV) were separated by taking advantage of their different solubilities either in alcohol [1 g. of (III) dissolves in 100 ml. of hot alcohol; 1 g. of (IV) in 2 ml.] or in aqueous acetic acid, in which only the stronger base (IV) dissolved. This experiment yielded 1·4 g. of (III) and 7·0 g. of (IV). It is important to use pure zinc in the Clemmensen reduction. Some samples of zinc used contained traces of sulphur, which was reduced to hydrogen sulphide and this, with compound (IV), gave a *substance*, m. p. 222—223° (Found : C, 72·6; H, 5·6; N, 10·2; S, 6·0. $C_{32}H_{32}O_2N_4S$ requires C, 71·6; H, 6·0; N, 10·4; S, 6·0%). This compound was readily separated from (III) and (IV), being only slightly soluble in boiling dilute aqueous acetic acid. It crystallised well from butanol. Its structure is being investigated.

10-*Keto*-1 : 6-*diaza*-3 : 4-8 : 9-*dibenzo*bicyclo[5 : 3 : 0]*deca*-3 : 8-*diene* (III). From ethanol, benzene, or ethyl acetate this compound separated in fine colourless needles, m. p. 254—255° (decomp.). It sublimed unchanged at 190—200°/1 mm. [Found : C, 77·0; H, 5·8; N, 11·3; *M* (in camphor), 251. $C_{16}H_{14}ON_2$ requires C, 76·8; H, 5·6; N, 11·2%; *M*, 250]. Hydrochloric acid dissolved (III), and with immediate cooling the *hydrochloride* separated. Recrystallised from ethanol, it formed colourless needles (m. p. 273—276°, decomp.) containing one molecule of water of crystallisation (Found : N, 9·1; loss at 110°, 5·6. $C_{16}H_{15}ON_2Cl,H_2O$ requires N, 9·1; H_2O, 5·9. Found, in dried salt : N, 9·8; Cl, 11·9. $C_{16}H_{15}ON_2Cl$ requires N, 9·7; Cl, 12·3%). The ketone (III) was stable in boiling alcoholic potassium hydroxide. The *benzoyl* derivative, readily obtained under Schotten–Baumann conditions, formed from ethanol colourless rhombs (m. p. 168·5—169·5°) (Found : C, 78·3; H, 5·4; N, 7·9. $C_{23}H_{18}O_2N_2$ requires C, 78·0; H, 5·1; N, 7·9%). An *acetyl* derivative was formed in boiling acetic anhydride and precipitated with water; it formed colourless needles (from 40% methanol), m. p. 193·5—194° (Found : C, 74·0; H, 5·4; N, 9·6. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5; N, 9·6%). A toluene-*p*-sulphonyl derivative could not be obtained. The *nitroso*-derivative was obtained by cooling a 3% solution of (III) in glacial acetic acid to 10° and adding the theoretical amount of sodium nitrite in twice its weight of water. After 2 hours, dilution with water precipitated the nitroso-compound in nearly theoretical yield. It crystallised from chloroform and ether in pale yellow, thin, hexagonal plates, or from *n*-butanol in stout prisms, m. p. 204° (Found : C, 69·3; H, 4·7; N, 15·0. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%). This compound gave the Liebermann nitroso-reaction. Short hydrolysis with either hot hydrochloric acid or 10% alcoholic sodium hydroxide yielded (III), together with some oily by-products.

Hydrolysis of (III).—Complete hydrolysis was achieved by refluxing for 12 hours with 6N-hydrochloric acid. The acid was then removed by evaporation under reduced pressure and desiccation completed by addition of alcohol containing a little hydrochloric acid, evaporation, and repeating this process once. The crystalline ωω′-diamino-*o*-xylene dihydrochloride hemihydrate was then separated from the oily product by addition of ethanol containing a drop of

hydrochloric acid, and collection and washing of the crystals with a little ethanol; the yield, from 3 g. of (III), was 2·5 g. (theory, 2·62 g.). The hydrochloride [m. p. 310° (decomp.)] was identified by conversion into the dibenzoyl derivative (m. p. and mixed m. p. 189—190°) and the dibenzenesulphonyl derivative (m. p. and mixed m. p. 125—126°). The alcoholic solution of the oily product on evaporation gradually gave crystalline 3-ethoxyphthalide (yield, 1·7 g.; theory, 2·1 g.), which had m. p. 69—70° after crystallisation from light petroleum containing 3% of ethanol. It was identified by mixed m. p. and by conversion into phthalazone and the anil of phthalaldehydic acid. These two compounds are as conveniently prepared from 3-ethoxyphthalide as from phthalaldehydic acid.

Phthalazone. 3-Ethoxyphthalide (0·36 g.), hydrazine sulphate (0·26 g.), sodium acetate (0·6 g.), and water (25 ml.) were heated under reflux (1 hour). From the solution, decolorised with a little charcoal, colourless needles of phthalazone (0·16 g.) separated on cooling (m. p. and mixed m. p. 182—183°).

Anil of phthalaldehydic acid. The anil was precipitated in crystalline form (yield 0·11 g.) when 3-ethoxyphthalide (0·1 g.), aniline (0·1 ml.), acetic acid (0·15 ml.), and water (12 ml.) were refluxed for 5 minutes (m. p. and mixed m. p. 179—180° after crystallisation from ethanol).

The following new derivatives of ωω′-diamino-*o*-xylene were prepared : *ditoluene*-p-*sulphonyl* (Schotten–Baumann), colourless prisms (from 50% methanol), m. p. 122·5—123·5° (Found : C, 59·8; H, 5·4; N, 6·0. $C_{22}H_{24}O_4N_2S_2$ requires C, 59·4; H, 5·4; N, 6·3%); *dipicrate* (from water), m. p. 242—244° (decomp.) (Found : C, 40·6; H, 3·2; N, 19·0. $C_{20}H_{18}O_{14}N_8$ requires C, 40·4; H, 3·1; N, 18·9%).

N-o-*Aminomethylbenzylphthalimidine* (IV).—This compound is dimorphous. It crystallised from benzene or benzene–ether in needles, m. p. 108·5—109°, or in stout rhombs, m. p. 120—121°. Both were pale cream in colour. By inoculation either form could be obtained at will and, in absence of the high-melting form, the less stable lower-melting form kept indefinitely [Found : C, 76·3; H, 6·3; N, 11·1%; *M* (in camphor), 237. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·4; N, 11·1%; *M*, 252]. The *amine* was slightly soluble in water, readily soluble in ethanol, benzene, and chloroform, and almost insoluble in ether or light petroleum. It showed a strong blue fluorescence in ultra-violet light. It had a bitter taste. Although the two forms of the base appeared to be dimorphs, differing but little in stability, it is noteworthy that on benzoylation they gave corresponding dimorphous forms of the benzoyl derivative. The amine (IV) gave a salt with hydriodic acid, but otherwise was unaffected. It was gradually attacked by N-alcoholic potassium hydroxide, but the products of decomposition have not been identified. It decomposed slowly above its m. p.

The *hydrochloride* crystallised from ethanol in fine white needles, m. p. 243—245° (Found : C, 67·0; H, 5·9; N, 10·3; Cl, 12·6. $C_{16}H_{17}ON_2Cl$ requires C, 66·6; H, 5·9; N, 9·7; Cl, 12·3%). The *hydriodide* formed pale yellow needles (from ethanol), m. p. 236—238° (decomp.) (Found : C, 50·6; H, 4·7; N, 7·3. $C_{16}H_{17}ON_2I$ requires C, 50·5; H, 4·5; N, 7·4%). The *chloroaurate* formed bright yellow prisms (from ethanol), m. p. 224—226° (decomp.) (Found : C, 32·6; H, 3·0; N, 5·2; Au, 33·4. $C_{16}H_{17}ON_2Cl_4Au$ requires C, 32·4; H, 2·9; N, 4·7; Au, 33·3%).

The *diacetyl* derivative (m. p. 127·5—128·5°) was obtained by boiling (IV) with acetic anhydride (1 hour); from 40% ethanol, it separated in small colourless needles (Found : C, 70·6; H, 5·7; N, 8·3; Ac, 24·7. $C_{20}H_{20}O_3N_2$ requires C, 71·4; H, 6·0; N, 8·3; Ac, 25·6%). The diacetyl derivative was hydrolysed to the parent base (IV) by refluxing it (5 hours) with 6N-hydrochloric acid. Benzoylation of the low-melting form under Schotten–Baumann conditions, or in pyridine, gave a *benzoyl* derivative of m. p. 185°, and like treatment of the high-melting form gave first a benzoyl derivative of m. p. 197° but later the lower-melting material. From ethanol, the more soluble low-melting form separated in stout gable-ended prisms, and the high-melting form in fine white needles. The former was converted into the latter form at 188—190°, but conversion appeared to be incomplete and purification was effected by crystallisation from ethanol, leaving a few crystals undissolved. Conversion of the high- into the low-melting form resulted from prolonged boiling of an alcoholic solution to destroy all crystalline nuclei or by dissolution in chloroform and precipitation with light petroleum [Found : C, 77·4; H, 5·9; N, 7·9%; *M* (in camphor), 341. $C_{23}H_{20}O_2N_2$ requires C, 77·5; H, 5·7; N, 7·9%; *M*, 356]. Attempts to hydrolyse the benzoyl derivative failed.

The *benzenesulphonyl* derivative was prepared quantitatively from (IV) by using benzenesulphonyl chloride in pyridine at room temperature. From *n*-butanol (charcoal) it formed colourless prisms, m. p. 196·5—198° (Found : C, 67·6; H, 5·1; N, 6·6; S, 8·5. $C_{22}H_{20}O_3N_2S$ requires C, 67·3; H, 5·1; N, 7·1; S, 8·2%). The *toluene*-p-*sulphonyl* derivative, m. p. 173°, was obtained from either dimorph under Schotten–Baumann conditions, or in pyridine at room

temperature or at the b. p. It crystallised from methanol or chloroform–ether in stout rhombs and fluoresced a strong blue in ultra-violet light [Found : C, 67·7; H, 5·4; N, 6·6; S, 8·2%; *M* (in camphor), 415. $C_{23}H_{22}O_3N_2S$ requires C, 67·9; H, 5·5; N, 6·9; S, 7·9%; *M*, 406]. Both arylsulphonyl derivatives were insoluble in aqueous sodium hydroxide.

The 2 : 4-*dinitrophenyl* derivative was obtained by refluxing (2 hours) equimolecular amounts of (IV) and 2 : 4-dinitrochlorobenzene in ethanol solution with anhydrous sodium acetate and formed yellow needles, m. p. 205—207° (decomp.) from butanol (Found : C, 63·4; H, 4·3; N, 13·2. $C_{22}H_{18}O_5N_4$ requires C, 63·2; H, 4·3; N, 13·4%). The N-*phthaloyl* derivative was obtained by refluxing (1 hour) equimolar amounts of (IV) and phthalic acid in acetic acid, and precipitation with water. From butanol it crystallised in colourless, stout prisms, m. p. 206·5—208° (slight decomp.) (Found : C, 75·6; H, 4·6; N, 7·2. $C_{24}H_{18}O_3N_2$ requires C, 75·4; H, 4·7; N, 7·3%). The *benzylidene* derivative was obtained by refluxing (IV) for 1 hour with benzaldehyde (20% excess) in ethanol acidified with acetic acid. The product, obtained by removing the alcohol and making the solution alkaline, crystallised from benzene or 75% ethanol in colourless plates, m. p. 155·5—156·5° (slight decomp.) (Found : C, 81·0; H, 5·6; N, 8·1. $C_{23}H_{20}ON_2$ requires C, 81·2; H, 5·9; N, 8·2%). The *picrate*, obtained by mixing the components in alcohol and crystallisation from *n*-butanol, formed yellow needles, m. p. 240—241° (decomp.) (Found : C, 55·2; H, 3·8; N, 14·5. $C_{22}H_{19}O_8N_5$ requires C, 54·9; H, 4·0; N, 14·6%).

Clemmensen Reduction of (III).—A mixture of (III) (4·2 g.), amalgamated zinc (24 g.), ethanol (70 ml.), and concentrated hydrochloric acid (35 ml.) was refluxed (30 hours), and additional hydrochloric acid (75 ml.) added at 3-hourly intervals during the reaction. The products were worked up as already described, and 1·5 g. of unchanged (III) and 1·8 g. of (IV) were obtained. The latter melted at 117—119° and was identified by mixed m. p. and by conversion into the benzoyl derivative. No other products were isolated.

N-o-*Hydroxymethylbenzylphthalimidine* (V).—The reaction of (IV) with nitrous acid in acetic acid medium takes place readily at 0° or at room temperatures, but conversion into (V) is incomplete particularly at the lower temperature. The conversion can be completed by subsequently refluxing the reaction products with aqueous alkali. When the reaction was performed at 0° no crystalline (V) could be obtained without alkali treatment; at 20° some crystalline (V) could be obtained directly, but, always, refluxing with alkali improved the yield. Nitrogen is evolved during treatment with alkali and apparently the diazo-compound possesses appreciable stability under the reaction conditions used. The following method was adopted for the preparation of (V).

A solution of sodium nitrite (2·07 g., 0·03 mole) in water (9 ml.) was added during 5—10 minutes to a solution of (IV) (2·52 g., 0·01 mole) in acetic acid (20 ml.) and water (3 ml.) at 15—20° (cooling). After 12 hours the clear yellow solution was diluted with water (30 ml.), the separated oil extracted in benzene, the solution washed free from acid, the benzene removed on a water-bath, and the residue boiled (40 minutes) with 30% sodium hydroxide (70 ml.). The dark oil, after being washed free from alkali was dissolved in benzene, filtered from insoluble by-products, and concentrated to give a crystalline product (1·9 g.). From aqueous alcohol (charcoal), the *hydroxy*-compound formed colourless, stout prisms, m. p. 128·5—130° (Found : C, 76·2; H, 6·1; N, 5·7. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 6·0; N, 5·5%). The infra-red absorption spectrum of (V) in chloroform shows C=O vibration at 1671 cm.$^{-1}$ and a strong OH vibration at 3400 cm.$^{-1}$. The compound is stable to boiling alcoholic N-sodium ethoxide. The 3 : 5-*dinitrobenzoyl* derivative, prepared in pyridine at room temperatures, crystallised from *n*-butanol (charcoal) in flat yellow prisms, m. p. 194·5—196·5° (decomp.) (Found : C, 61·9; H, 3·9; N, 9·0. $C_{23}H_{17}O_7N_3$ requires C, 61·7; H, 3·8; N, 9·4%). The *benzylidene* derivative was prepared by refluxing (2 hours) (V) (0·25 g.) in alcohol (20 ml.) with benzaldehyde (5 drops) and 40% sodium hydroxide (4 drops), removing the alcohol, and washing the residual oil with water. The dried product slowly crystallised. It was boiled with benzene (5 ml.) and the crystalline residue (0·12 g.) was recrystallised from aqueous alcohol. It formed pale cream needles, m. p. 198—199° (decomp.) (Found : C, 80·7; H, 5·6; N, 4·4. $C_{23}H_{19}O_2N$ requires C, 80·9; H, 5·6; N, 4·1%).

N-o-*Chloromethylbenzylphthalimidine* (VI).—A mixture of (V) (2·5 g.), concentrated hydrochloric acid (30 ml.), and water (20 ml.) was refluxed for 8—10 hours (oil-bath), cooled, and diluted with water. The oil produced was washed, and crystallised when dried under reduced pressure. From aqueous alcohol it formed colourless, blade-shaped plates (1·82 g.), m. p. 119·5—121° (Found : C, 71·0; H, 5·2; N, 5·3; Cl, 12·6. $C_{16}H_{14}ONCl$ requires C, 70·7; H, 5·2; N, 5·2; Cl, 13·0%). Refluxing of this compound with 10% aqueous sodium carbonate for 5 hours regenerated (V) almost quantitatively. Its β-*naphthylamine* derivative was prepared by re-

fluxing it (4 hours) in alcohol with sodium acetate and a small excess of β-naphthylamine. After precipitation with water and drying, the crystalline product was digested with benzene to dissolve impurities and crystallised from *n*-butanol; it formed colourless plates, m. p. 194·5—195·5° (Found: C, 82·4; H, 5·7; N, 7·2. $C_{26}H_{22}ON_2$ requires C, 82·5; H, 5·9; N, 7·4%).

N-o-*Xylylphthalimidine* (VII).—(*a*) *N-o*-Xylylphthalimide, prepared according to Strassmann (*Ber.*, 1888, **21**, 576), had m. p. 150·5—151·5° (Strassmann gives m. p. 148—149°). For reduction, 2·5 g. were refluxed with concentrated hydrochloric acid (10 ml.), alcohol (15 ml.), and tin (1·6 g.), more acid (5 ml.) and tin (2·6 g.) being added during 2 hours. After 3·5 hours the clear solution was decanted from unchanged tin, excess of alcohol was evaporated, the residues were made strongly alkaline, and the N-o-*xylylphthalimidine* was extracted in benzene. The crude material, decolorised in alcoholic solution and crystallised from aqueous alcohol, then formed colourless needles, m. p. 95·5—96·5° (1·7 g.) (Found: C, 81·0; H, 6·3; N, 5·9. $C_{16}H_{15}ON$ requires C, 81·0; H, 6·4; N, 5·9%).

(*b*) A mixture of (VI) (0·27 g.), acetic acid (5 ml.), and zinc (0·2 g.) was refluxed, and during 2 hours more acetic acid (3 ml.) and zinc dust (0·3 g.) were added. After a further hour the unchanged zinc was filtered from the hot liquid and washed with hot alcohol (2 × 5 ml.), and the filtrate diluted with water (50 ml.) and left until the product crystallised (0·18 g.; m. p. 93—95°). After crystallisation it had a m. p. identical with the product from (*a*) and a mixed m. p. showed no depression. The infra-red spectrum of a Nujol suspension showed a C=O vibration band at 1686 $cm.^{-1}$, but no OH band.

Oximinophthalimide from o-*Phthalaldehydic Acid.*—Oximinophthalimide has been prepared from phthalaldehyde and hydroxylamine (Beilstein's "Handbuch," 4th edn., vol. 21, p. 460). It can equally well be prepared from *o*-phthalaldehydic acid or 3-ethoxyphthalide. When either of these compounds (0·5 g.) and hydroxylamine hydrochloride (1·5 g.), pyridine (7·5 ml.), and ethanol (7·5 ml.) were heated together on a water-bath for 3 hours, oximinophthalimide was the main product. It (0·25 g.), m. p. 262—264° (decomp.), was isolated by evaporating most of the solvent, pouring into ice-cold dilute hydrochloric acid, and crystallising the colourless precipitate from methanol (Found: C, 59·5; H, 3·6; N, 17·2. Calc. for $C_8H_6O_2N_2$: C, 59·3; H, 3·7; N, 17·3%). A mixed m. p. with a specimen prepared from *o*-phthalaldehyde showed no depression. The following derivatives appear to be new: o-*phthalaldehyde bis*-2 : 4-*dinitrophenylhydrazone*, small, bright orange needles (from *o*-dichlorobenzene), m. p. 278—280° (decomp.) (Found: C, 48·5; H, 2·9; N, 22·7. $C_{20}H_{14}O_8N_8$ requires C, 48·6; H, 2·9; N, 22·7%), and *bis*-p-*aminoazobenzene* derivative (separated as a crystalline precipitate when concentrated ethanolic solutions of *o*-phthalaldehyde and *p*-aminoazobenzene were mixed and left for 3 hours at room temperature), orange-brown crystals (from *n*-butanol), m. p. 196—197·5° (decomp.) (Found: C, 78·2; H, 4·9; N, 17·0. $C_{32}H_{24}N_6$ requires C, 78·0; H, 4·9; N, 17·1%); the 2 : 4-*dinitrophenylhydrazone of* *o*-phthalaldehydic acid, small orange needles (from *n*-butanol), m. p. 264—266° (decomp.) (Found: C, 51·2; H, 3·2; N, 17·0. $C_{14}H_{10}O_6N_4$ requires C, 50·9; H, 3·1; N, 17·0%).

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