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## Derivatives of 5,6,11,12-Tetrahydrodibenzo[*b*,*f*][1,4]diazocine and 5,6,11,12-Tetrahydrodibenzo[*b*,*f*][1,5]diazocine

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5,6,11,12-Tetrahydrodibenzo[b.f][1,4]diazocine reacts with paraformaldehyde to give the 5,12-endo-methanoderivative: similar bridged compounds were prepared from aromatic aldehydes, but not ketones. The 5,12-endomethano-derivative is comparable to Tröger's base in its reactions. The synthesis of N-alkyl-5,6,11,12-tetrahydrodibenzo[b.f][1,5]diazocines and N-alkyl-5,6,11,12-tetrahydrodibenzo[b.f][1,4]diazocines by direct alkylation and by acylation and subsequent reduction has been investigated. An N-amino- and an NN'-diaminoderivative of the [1,5]diazocine were prepared.

THE synthesis of Tröger's base (5,6,11,12-tetrahydro-2,8-dimethyl-5,11-endo-methanodibenzo[b,f][1,5]diazo-

cine) (I;  $\mathbb{R}^1 = \mathbb{M}e$ ,  $\mathbb{R}^2 = \mathbb{R}^3 = \mathbb{H}$ ) from p-toluidine and formaldehyde in acid solution, and the extension of this synthesis to analogues, has been described in a number of papers.<sup>1</sup> Cooper and Partridge<sup>2</sup> synthesised the 5,6,11,12-tetrahydrodibenzo[b,f][1,5]diazocines (II;  $\mathbb{R}^1 = \mathbb{M}e$  or H,  $\mathbb{R}^2 = \mathbb{H}$ ), and showed that they reacted with aldehydes and certain other carbonyl compounds to give derivatives of the Tröger's base type, the product from (II;  $\mathbb{R}^1 = \mathbb{M}e$ ,  $\mathbb{R}^2 = \mathbb{H}$ ) and formaldehyde being identical with Tröger's base.

<sup>1</sup> (a) J. Tröger, J. prakt. Chem., 1887, **36**, 227; (b) M. A. Spielman, J. Amer. Chem. Soc., 1935, **57**, 583; (c) T. R. Miller and E. C. Wagner, *ibid.*, 1941, **63**, 832; (d) L. I. Smith and W. M. Schubert, *ibid.*, 1948, **70**, 2656; (e) M. Haring, Helv. Chim. Acta, 1963, **46**, 2970.

<sup>2</sup> F. C. Cooper and M. W. Partridge, J. Chem. Soc., 1955, 991.

Little attention has been paid to the isomeric dibenzo-[b,f] [1,4] diazocine ring system.<sup>3</sup> Schroth and Streckenbach <sup>3d</sup> have reported, without giving experimental details, the synthesis of 5,6,11,12-tetrahydro-5,12-dimethyldibenzo[b, f][1,4]diazocine (IIIa) by the inter-*NN'*-dimethyl-*o*-phenylenediamine action of and aa'-dibromo-o-xylene: the 5,12-bis-p-tolylsulphonyl derivative (IIIb) was also prepared from NN'-bis-p-tolylsulphonyl-o-phenylenediamine, and hydrolysed with hydrogen bromide in glacial acetic acid to the free base (III; R = H). Experimental details for these syntheses now appear in this paper. The free base (III; R = H) and the 5,12-bis-p-tolyl-sulphonyl derivative (IIIb) are

<sup>3</sup> (a) J. Thiele and K. G. Falk, Annalen, 1906, **347**, 112; (b) M. V. Betrabet and G. C. Chakravarti, J. Indian Chem. Soc., 1930, **7**, 495; (c) H. Stetter, L. Marx-Moll, and H. Rutzen, Chem. Ber., 1958, **91**, 1775; (d) W. Schroth and B. Streckenbach, Z. Chem., 1963, **3**, 465. Org.

found to have m.p's of 190—192 and 192—193° respectively, and not 198 and 178° as previously reported. The base (III; R = H) gave diacetyl (IIIc), dibenzoyl (IIId), and dinitroso- (IIIe) derivatives with acetic anhydride, benzoyl chloride, and nitrous acid respectively.

5,6,11,12-Tetrahydrodibenzo[b,f][1,4]diazocine (III; R = H) reacted with paraformaldehyde in boiling



xylene to yield the 5,12-endo-methano-derivative (IV)  $\mathbf{R} = \mathbf{H}$ ). Similar bridged compounds (IV a-g) prepared in good yield from were aromatic aldehydes, but the ketones acetone, cyclohexanone, acetophenone, and N-methyl-4-piperidone failed to react. The reactions of the 5,12-endo-methano-derivative (IV; R = H) were comparable to those of Tröger's base 1b in that treatment with acetic anhydride or nitrous acid resulted in loss of the endo-methano-bridge and the formation of 5,12-diacetyl- (IIIc) and 5,12-dinitroso-(IIIe) derivatives. Likewise, reaction of the endo-methano-derivative (IV; R = H) with dimethyl sulphate and sodium hydroxide solution<sup>4</sup> by Häring's method 1e afforded 5,6,11,12-tetrahydro-5-methyldibenzo[b,f][1,4]diazocine (VI; R = H), which was characterised as the nitroso- (VIa) and acetyl (VIb) derivatives.

Häring <sup>1e</sup> has prepared 3-dimethylaminopropyl derivatives of 5,6,11,12-tetrahydrodibenzo[b,f][1,5]diazocines (II) by treating the sodio-derivative, prepared with sodamide in xylene, with 3-dimethylaminopropyl chloride. This method has proved of limited use for the preparation of alkyl derivatives since although the dibenzo[b,f][1,5]diazocine (V; R = H) gave the 11-benzyl derivative (Vc) with benzyl bromide, with phenethyl bromide,  $\gamma$ -chlorobutyrophenone, or 1-bromo-3-chloropropane starting material was recovered. Furthermore, the dibenzo[b,f][1,4]diazocine (VI; R = H) failed to react with 3-dimethylaminopropyl chloride under these conditions.

The preparation of alkyl derivatives by reduction by lithium aluminium hydride of the corresponding amides is also of limited value. The dibenzo[b,f][1,5]diazocine (V; R = H) reacted with acetic anhydride, phenylacetyl chloride, bromoacetyl bromide, and 3-bromopropanoyl chloride to give the corresponding acyl derivatives (V; b, d—f). Interaction of the bromoacetyl and bromopropanoyl derivatives with piperidine or morpholine afforded the acyl derivatives (Vg—j). The acetyl group of the amide (Vb) was reduced to an ethyl group with lithium aluminium hydride, but reduction of the phenylacetyl derivative (Vd) and the piperidino- and morpholino-compounds furnished viscous oils which, from their i.r. spectra, probably contained unchanged starting material: crystallisation of these oils from light petroleum gave up to 30% of the free amine



(V;  $\mathbf{R} = \mathbf{H}$ ), formed by complete loss of the acyl sidechain. The piperidinopropionyldibenzo[b, f][1,4]diazocine (VIc) gave a similar mixture on reduction with lithium aluminium hydride.

The reduction of the dinitrosodibenzo[b,f][1,5]diazocine (II;  $\mathbb{R}^1 = \mathrm{Me}$ ,  $\mathbb{R}^2 = \mathrm{NO}$ ) to the free base (II;  $\mathbb{R}^1 = \mathrm{Me}$ ,  $\mathbb{R}^2 = \mathrm{H}$ ),<sup>4</sup> and to 4-amino-*m*-xylene,<sup>1b</sup> has been reported. The dinitroso-derivative (II;  $\mathbb{R}^1 = \mathrm{Me}$ ,  $\mathbb{R}^2 = \mathrm{NO}$ ) has now been converted into the diaminoderivative (II;  $\mathbb{R}^1 = \mathrm{Me}$ ,  $\mathbb{R}^2 = \mathrm{NH}_2$ ) by reduction with zinc and acetic acid. Interaction of the dibenzo-[b,f][1,5]diazocine (V;  $\mathbb{R} = \mathrm{H}$ ) and nitrous acid afforded a nitroso-derivative (Va) which was reduced to the corresponding amino-compound.

## EXPERIMENTAL

I.r. spectra were determined on Nujol mulls below 2500 cm.<sup>-1</sup>, and solutions in carbon tetrachloride above 2500 cm.<sup>-1</sup>, with a Unicam spectrophotometer, model SP 200G. 5,6,11,12-*Tetrahydro*-5,12-*dimethyldibenzo*[b,f][1,4]*diazo*-

cine (IIIa).—A mixture of NN'-dimethylatochar[0,3][2,1]attaso amine (I g., I mol.),  $\alpha\alpha'$ -dibromo-o-xylene (2·14 g., I·1 mol.), anhydrous potassium carbonate (2·1 g.), and dry toluene (25 ml.) was heated under reflux in an oil-bath for 4 hr., filtered hot, and the solvent removed under reduced pressure. The residue, recrystallised twice from ethanol, afforded the dibenzodiazocine (0·85 g.) as needles, m.p.

<sup>4</sup> F. C. Cooper and M. W. Partridge, J. Chem. Soc., 1957, 2888.

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128–130° (lit., <sup>3d</sup> 131°) (Found: C, 80·4; H, 7·8; N, 12·2. Calc. for  $C_{16}H_{18}N_2$ : C, 80·6; H, 7·6; N, 11·8%);  $\lambda_{max}$ : (in ethanol) 234, 278, and 312 mµ (log  $\varepsilon$  4·47, 3·90, and 3·76);  $\nu_{max}$ . 2800 cm.<sup>-1</sup> (NMe).

5,6,11,12-Tetrahydro-5,12-bis-p-tolylsulphonyldibenzo[b,f]-[1,4]diazocine (IIIb).—NN'-Bis-p-tolylsulphonyl-o-phenylenediamine (62·4 g., 1 mol.),  $\alpha\alpha'$ -dibromo-o-xylene (43·5 g., 1·1 mol.), and anhydrous potassium carbonate (42·0 g.) were heated under reflux in dry toluene (750 ml.) for 4 hr. in an oil-bath. Charcoal was added and the mixture was filtered hot and concentrated to 400 ml. The substituted diazocine (65·8 g., 85%) which separated from the cooled solution crystallised from toluene as prisms (Found: C, 64·8; H, 5·05; N, 5·3. Calc. for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 64·85; H, 5·05; N, 5·4%). This compound had m.p. 192—193°, whereas Schroth and Streckenbach <sup>2d</sup> record 178°.

5,6,11,12-Tetrahydrodibenzo[b,f][1,4]diazocine (III; R = H).—The bis-p-tolylsulphonyl derivative (IIIb) (72 g.) and phenol (52 g.) were stirred together in 50% (w/w) hydrogen bromide in glacial acetic acid (580 ml.) at 50° for 24 hr.

with Aldehydes and Ketones.—A solution of the base (III; R = H) (1 g.) and the aldehyde in xylene (40 ml.) was heated under reflux for 1 hr. (16 hr. with paraformaldehyde) and evaporated to dryness under reduced pressure on a steam-bath; the residue was crystallised from a suitable solvent. The compounds so prepared, all of which were colourless, are listed in the Table.

Compound (IV; R = H)  $\lambda_{max}$  (in ethanol) 282 mµ (log  $\varepsilon$  3·31),  $\lambda_{max}$  (in ethanol containing 1% 10n-hydrochloric acid) 247 mµ (log  $\varepsilon$  3·84). Compound (IVa)  $\lambda_{max}$  (in ethanol) 286 mµ (log  $\varepsilon$  3·31).

No reaction occurred when the base (III; R = H) was heated under reflux in acetone or in cyclohexanone, or in xylene with either acetophenone or *N*-methyl-4-piperidone.

Reactions of 5,6,11,12-Tetrahydro-5,12-endo-methanodibenzo[b,f][1,4]diazocine.—(a) The endo-methano-compound (IV; R = H) (0.5 g.), when heated under reflux for 1 hr. in acetic anhydride (5 ml.), gave the diacetyldibenzodiazocine (IIIc) (0.32 g., 50%), m.p. and mixed m.p. 233— 235°.

5,12-endo-Substituted-5,6,11,12-tetrahydrodibenzo[b,f,][1,4]diazocines (IV)

	Aldehvde	Solvent for	Yield			Found (%)			Required (%)			
(IV)	(mol.)	crystn.*	Form	М.р.	(%)	Formula	С	н	N	С	$\mathbf{H}$	Ν
(IV; R = H)	4	Pet	Needles	109-110°	75	$C_{15}H_{14}N_{2}$	81.05	6.3	12.75	81.1	6.35	12.6
a	<b>2</b>	EtOH	Spars	203 - 205	81	$C_{21}H_{18}N_{2}$	84.7	$6 \cdot 2$	9.7	84.5	6.1	$9 \cdot 3$
b	$1 \cdot 2$	PhMe	Prisms	207 - 208	90	C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>	73.5	4.8	12.1	73.4	5.0	12.2
с	1.5	PhH	Prisms	221 - 223 +	80	$C_{21}H_{12}N_{2}O$	80.2	6.0	9.05	80.2	5.8	8.9
d	$1 \cdot 2$	PhH	Plates	185	80	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	77.05	6.1	8.1	76.7	5.85	8.1
е	1.3	EtOH	Prisms	191 - 192	44	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O	<b>79</b> ·0	5.7	9.8	79.1	5.6	9.7
f	1.5	EtOH	Needles	189—191†	62	C19H15N3O3	68.2	4.4	12.7	68.5	4.5	12.6
g	$1 \cdot 2$	EtOH	Prisms	192	<b>54</b>	$C_{20}H_{17}N_3$	<b>80</b> ∙0	$5 \cdot 8$	14.2	$80 \cdot 2$	5.7	<b>14</b> ·0

\* Pet = light petroleum (b.p.  $60-80^{\circ}$ ). † Decomp.

The mixture was set aside at room temperature for 2 days; the precipitate was washed with a little glacial acetic acid and dissolved in boiling water. Charcoal was added and the solution was filtered and basified with sodium hydroxide solution. Crystallisation of the precipitate from toluene afforded the tetrahydrodibenzodiazocine (19.6 g., 67%) as prisms, m.p. 190—192° (lit.,<sup>3d</sup> 198°) (Found: C, 79.8; H, 6.8; N, 13.3. Calc. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 79.95; H, 6.7; N, 13.3%);  $\lambda_{max}$  (in ethanol) 222, 257, and 305 (log  $\varepsilon$  4.50, 3.71, and 3.60),  $\lambda_{max}$  (in ethanol containing 1% 10N-hydrochloric acid) 249 and 294 m $\mu$  (log  $\varepsilon$  3.97 and 3.27);  $\nu_{max}$ . 3410 (NH) cm.<sup>-1</sup>.

The diacetyl derivative (IIIc) (85%), prepared by heating the base (III; R = H) in refluxing acetic anhydride, separated from ethanol as plates, m.p. 229–231° (Found: C, 73.4; H, 6.2; N, 9.4.  $C_{18}H_{18}N_2O_2$  requires C, 73.5; H, 6.2; N, 9.5%).

The dibenzoyl derivative (IIId) (70%) was prepared by reaction of the base (III; R = H) and benzoyl chloride in a mixture of benzene and pyridine; it crystallised from ethanol as plates, m.p. 237–239° (Found: C, 80.5; H, 5.7; N, 6.6.  $C_{28}H_{22}N_2O_2$  requires C, 80.35; H, 5.3; N, 6.7%).

The dinitroso-derivative (IIIe) was prepared by addition of sodium nitrite (0.82 g.) in water (30 ml.) dropwise at 0° to a solution of the base (III; R = H) (1 g.) in 10N-hydrochloric acid (4 ml.) and ethanol (20 ml.). Crystallisation of the precipitate from toluene afforded the *dinitrosoderivative* (0.95 g., 74%) as pale yellow prisms, m.p. 214— 217° (decomp.) (Found: C, 63.0; H, 4.7; N, 20.6.  $C_{14}H_{12}N_4O_2$  requires C, 62.7; H, 4.5; N, 20.9%).

Reaction of 5,6,11,12-Tetrahydrodibenzo[b,f][1,4]diazocine

(b) When treated with nitrous acid in aqueous ethanol, the *endo*-methano-compound gave the dinitrosodibenzodiazocine (IIIe) (80%), m.p. and mixed m.p.  $215-218^{\circ}$  (decomp.).

(c) 5,6,11,12-Tetrahydro-5-methyldibenzo[b,f][1,4]diazocine (VI; R = H). Dimethyl sulphate (13.6 g., 1.2 mol.) in anhydrous benzene (40 ml.) was added with cooling to a solution of the 5,12-endo-methano-compound (20.0 g., 1 mol.) in benzene (80 ml.), and the mixture was heated under reflux for 15 min. on a water-bath. The precipitate was washed with anhydrous benzene, dried at 100°, and dissolved in water (120 ml.), the solution being boiled to drive off any residual benzene. The solution was kept warm to prevent crystallisation and added dropwise during 30 min. to a well-stirred mixture of 2N-sodium hydroxide solution (120 ml.) and ice. The mixture was stirred for 1 hr. and then set aside overnight. Crystallisation of the precipitate from light petroleum (b.p. 100-120°) (400 ml.) gave the methyldibenzodiazocine (9.6 g., 48%) as needles, m.p. 192-194° (decomp.) (Found: C, 80.95; H, 6.8; N, 12.45.  $C_{15}H_{16}N_2$  requires C, 80.4; H, 7.2; N, 12.5%),  $\lambda_{max}$ . (in ethanol) 229, 269, and 308 m $\mu$  (log  $\varepsilon$  4.46, 3.83, and 3.66),

 $v_{max}$  3415 (N-H), and 2800 (N-Me) cm.<sup>-1</sup>. The N-nitroso-derivative (VIa). Sodium nitrite (0.4 g.) in water (15 ml.) was added to a solution of the base (VI; R = H) (1 g.) in 10N-hydrochloric acid (2 ml.) and ethanol (10 ml.) at 0°. After 15 min. the precipitated N-nitrosoderivative (0.59 g., 52%) was crystallised from ethanol to give pale yellow plates, m.p. 144—146° (Found: C, 71.0; H, 6.1; N, 16.85. C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O requires C, 71.2; H, 6.0; N, 16.6%).

The acetyl derivative (VIb), prepared by heating the base

under reflux with acetic anhydride, crystallised from light petroleum (b.p. 80—100°) as prisms, m.p. 110—112° (Found: C, 76·6; H, 6·8.  $C_{17}H_{18}N_2O$  requires C, 76·6; H, 6·8%).

11-Benzyl-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo[b,f]-[1,5]diazocine (Vc).—The dibenzodiazocine (V; R = H) (10 g., 1 mol.) and sodamide (2.03 g., 1.3 mol.) were heated gently and stirred under reflux in toluene (50 ml.) for 2.5 hr. in an atmosphere of nitrogen. Benzyl bromide (8.15 g., 1.2 mol.) was added to the cooled slurry of the precipitated sodio-derivative, and the mixture was heated under reflux for 1 hr., filtered hot, and evaporated to dryness. Crystallisation of the residue from ethanol gave the benzyldibenzo-[b,f][1,5]diazocine (8.15 g., 60%) as prisms, m.p. 130— 132° (Found: C, 84.3; H, 7.4; N, 8.3.  $C_{24}H_{26}N_2$  requires C, 84.2; H, 7.65; N, 8.2%).

Other Attempted Alkylations.—When phenethyl bromide,  $\gamma$ -chlorobutyrophenone, or 1-bromo-3-chloropropane was substituted for benzyl bromide in the foregoing synthesis, starting material was recovered. The dibenzo-[b,f][1,4]diazocine (VI; R = H) failed to react with 3-dimethylaminopropyl chloride under these conditions.

11-Acyl-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo[b,f]-[1,5]diazocines.— 11-Acetyl-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo[b,f][1,5]diazocine (Vb) (9·3 g., 80%), obtained when the base (V; R = H) (10 g.) was heated under reflux with acetic anhydride, gave prisms, m.p. 171— 173° (ethanol) (Found: C, 77·45; H, 7·4; N, 9·35.  $C_{19}H_{22}N_2O$  requires C, 77·5; H, 7·5; N, 9·5%).

11-Bromoacetyl-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo-[b,f][1,5]diazocine (Ve). A solution of the base (V; R = H) (40·3 g., 1 mol.) and pyridine (14·1 g., 1·1 mol.) in toluene (240 ml.) was cooled in ice and stirred whilst bromoacetyl bromide (35·4 g., 1·1 mol.) in toluene (40 ml.) was added dropwise, rapidly. The mixture was heated under reflux for 15 min., cooled, and shaken with water (100 ml.). Evaporation of the toluene and crystallisation of the residue from light petroleum (b.p. 80—100°) afforded the bromoacetyl derivative (42·3 g., 71%) as prisms, m.p. 144—146° (Found: C, 61·5; H, 5·5; N, 7·3.  $C_{19}H_{21}BrN_2O$  requires C, 61·1; H, 5·7; N, 7·5%).

11-(3-Bromopropanoyl)-5,6,11,12-tetrahydro-2,5,8-tri-

methyldibenzo[b,f][1,5]diazocine (Vf) (71%), prepared analogously from the base (V; R = H) and 3-bromopropanoyl chloride, separated from light petroleum (b.p.  $100-120^{\circ}$ ) as prisms, m.p.  $112-114^{\circ}$  (Found: N, 7.5.  $C_{20}H_{23}BrN_2O$  requires N, 7.2%).

5,6,11,12-Tetrahydro-2,5,8-trimethyl-11-phenylacetyldibenzo[b,f][1,5]diazocine (Vd) (77%), prepared analogously from the base (V; R = H) and phenylacetyl chloride, crystallised from ethanol as prisms, m.p. 111–113° (Found: N, 7.5.  $C_{25}H_{26}N_2O$  requires N, 7.6%).

5,6,11,12-Tetrahydro-2,5,8-trimethyl-11-piperidinoacetyldibenzo[b,f][1,5]diazocine (Vg). The bromoacetyl derivative (Ve) (15.0 g., 1 mol.) and piperidine (10.5 g., 3 mol.) were heated under reflux in ethanol (75 ml.) for 1 hr. The cooled solution was diluted with water (300 ml.) and extracted with benzene. Evaporation of the solvent, and crystallisation of the residue from light petroleum (b.p. 60-80°, 25 ml.) gave the piperidinoacetyl derivative (10.5 g., 69%) as plates, m.p. 107-109° (Found: C, 76.1; H, 8.4; N, 10.9.  $C_{24}H_{31}N_3O$  requires C, 76.35; H, 8.3; N, 11.1%). The following derivatives of the dibenzo[b,f][1,5]diazocine (V; R = H) were prepared analogously:

The morpholinoacetyl derivative (Vh) (84%), prisms from light petroleum (b.p. 60-80°) m.p. 100-101° (Found:

C, 72.6; H, 7.7; N, 11.3.  $C_{23}H_{29}N_3O_2$  requires C, 72.8; H, 7.7; N, 11.1%).

The 3-piperidinopropanoyl derivative (Vi) (81%), plates from light petroleum (b.p.  $80-100^{\circ}$ ), m.p.  $110-112^{\circ}$ (Found: C, 76.65; H, 8.5; N, 10.6.  $C_{25}H_{33}N_{3}O$  requires C, 76.7; H, 8.5; N, 10.7%).

The 3-morpholinopropanoyl derivative (Vj) (62%), prisms, m.p. 128–129° after two crystallisations from light petroleum (b.p. 80–100°) (Found: C, 73·5; H, 8·1; N, 11·0.  $C_{24}H_{31}N_3O_2$  requires C, 73·2; H, 7·9; N, 10·7%).

12-(3-Bromopropanoyl)-5,6,11,12-tetrahydro-5-methyldibenzo[b,f][1,4]diazocine (VId).—This was prepared from the base (VI; R = H) (15.9 g.) and 3-bromopropanoyl chloride (13.4 g.) by the method used for the bromopropanoyl compound (Vf). The crude product was heated under reflux with light petroleum (b.p. 80—100°; 90 ml.) (charcoal). The 12-(3-bromopropanoyl) derivative (4.9 g., 19%) was deposited from the filtrate as plates, m.p. 106—108° (Found: C, 60.7; H, 5.3; N, 7.7. C<sub>18</sub>H<sub>19</sub>BrN<sub>2</sub>O requires C, 60.25; H, 5.3; N, 7.8%),  $\lambda_{max}$  (in ethanol) 261 and 305 m $\mu$  (log  $\varepsilon$  4.03 and 3.52),  $v_{max}$ . 1655 cm.<sup>-1</sup> (amide I). 5,6,11,12-Tetrahydro-5-methyl-12-(3-piperidinopropanoyl)-

5,6,11,12-Tetrahydro-5-methyl-12-(3-piperidinopropanoyl)dibenzo[b,f][1,4]diazocine (VIc).—This was prepared from thebromopropanoyl compound (VId) and piperidine, by the general method described earlier; it was obtained as prisms (75%), m.p. 96—97° (Found: C, 75.8; H, 8.1; N, 11.6.  $C_{23}H_{29}N_3O$  requires C, 76.0; H, 8.05; N, 11.6%),  $\lambda_{max}$  (in ethanol) 260 and 306 mµ (log  $\varepsilon$  4.04 and 3.53),  $\nu_{max}$  2945 (CH<sub>2</sub>) and 1650 (amide I) cm.<sup>-1</sup>. Reduction of Acyltetrahydrodibenzodiazocines.—11-Ethyl-

Reduction of Acyltetrahydrodibenzodiazocines.—11-Ethyl-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo[b,f][1,5]diazocine. —The acetyldibenzodiazocine (Vb) (2 g., 1 mol.) was heated under reflux in anhydrous ether (100 ml.) and lithium aluminium hydride (0·19 g., 0·6 mol.) suspended in ether (20 ml.) was added during 15 min. The mixture was heated for 2 hr., cooled, and shaken with sodium hydroxide solution. Evaporation of the ether and crystallisation of the residue from ethanol gave the 11-ethyl derivative (1·1 g., 58%) as prisms, m.p. 129—131° (Found: C, 81·4; H, 8·6; N, 9·9.  $C_{19}H_{24}N_2$  requires C, 81·4; H, 8·6; N, 10·0%).

Similar reduction of the phenylacetyl (Vd), alkylaminoacetyl (Vg) and (Vh), and alkylaminopropionyl (Vi) and (Vj) derivatives gave viscous oils which, from their i.r. spectra, were shown usually to contain starting material; on crystallisation from light petroleum they gave up to 30% of the free base (V; R = H).

Reduction of the piperidinopropionyldibenzo[b, f][1,4]diazocine (VIc) with lithium aluminium hydride gave a similar mixture.

5,6,11,12-Tetrahydro-2,5,8-trimethyl-11-nitrosodibenzo-

[b,f][1,5] diazocine (Va).—A solution of the base (V; R = H) in ethanolic hydrochloric acid was treated with aqueous sodium nitrite solution. After 10 min. the mixture was basified, and the precipitate crystallised from ethanol to yield the N-nitroso-compound (84%) as cream plates, m.p. 165—167° (Found: C, 72·2; H, 7·0; N, 15·0.  $C_{17}H_{19}N_3$ requires C, 72·6; H, 6·8; N, 14·9%).

11-Amino-5,6,11,12-tetrahydro-2,5,8-trimethyldibenzo-[b,f]-[1,5]diazocine (V;  $R = NH_2$ ).—The foregoing nitrosocompound (Va) (5 g.) and zinc dust (16.0 g.) were suspended in 90% ethanol (40 ml.). Aqueous acetic acid (50%, 50 ml.) was added, and the mixture was vigorously stirred at 50° for 15 min., it was then filtered hot. (Heating of the mixture for longer periods or at a higher temperature, resulted in lower yields and impure products). The filtrate was kept at 0° overnight, filtered, and evaporated to dryness under reduced pressure on a steam-bath. The residue was triturated with dilute sodium hydroxide solution, washed with water, and crystallised from ethanol. The *substituted hydrazine* (2·2 g., 46%) was obtained as prisms, m.p. 142— 144° (Found: C, 75·9; H, 8·0; N, 16·0.  $C_{17}H_{21}N_3$  requires C, 76·35; H, 7·9; N, 15·7%).

5,11-Diamino-5,6,11,12-tetrahydro-2,8-dimethyldibenzo-

[b,f][1,5] diazocine (II;  $R^1 = Me$ ,  $R^2 = NH_2$ ) was prepared analogously from the dinitroso-compound (II;  $R^1 = Me$ ,  $R^2 = NO$ ) (5 g.) by using twice the above quantities of zinc, ethanol, and acetic acid. The diamino-compound (0.80 g., 18%) separated from ethanol as plates, m.p.  $190-192^{\circ}$  (Found: C, 71.6; H, 7.45; N, 20.7.  $C_{16}H_{20}N_4$  requires C, 71.6; H, 7.5; N, 20.9%).

Reduction of the nitroso-compound (Va) or dinitrosocompound (II;  $R^1 = Me$ ,  $R^2 = NO$ ) with lithium aluminium hydride gave no identifiable product.

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