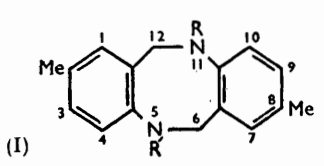
564. *Cyclic Amidines. Part V.** 5 : 11-endo-*Substituted* 5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethylphenhomazines.*

By F. C. Cooper and M. W. Partridge.

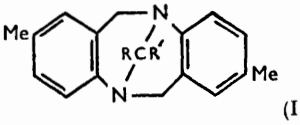
The replacement of the 5 : 11-*endo*methylene bridge in Tröger's base has been examined. 5 : 11-*endo*-Substituted analogues are readily formed by condensation of carbonyl compounds and 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethylphenhomazine. The only other type of bridge introduced was 5 : 11-*endo*ethoxymethylene.

Hitherto 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethylphenhomazine (I; R = R′ = H) has been obtainable only in small yield from methyl 5-methylanthranilate.[1] Although Spielman [2] found that the *endo*methylene group in Tröger's base underwent replacement on acylation or nitrosation, he was unable to convert the resulting compounds (I; R = R′ = Ac, Bz, or NO) into the disecondary base (I; R = R′ = H). The dinitroso-derivative (I; R = R′ = NO) in acetic acid has now been converted into the required base (I; R = R′ = H) in high yield by treatment with cuprous chloride in hydrochloric acid.[3] 5 : 6 : 11 : 12-Tetrahydro-2 : 8-dimethylphenhomazine thus becomes available in good overall yield from *p*-toluidine *via* Tröger's base.[4]

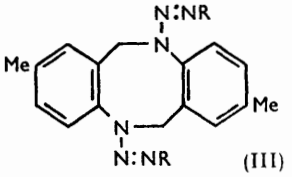
Methylation of Tröger's base with methyl sulphate and alkali resulted in the fission of the *endo*methylene bridge and furnished the methyl derivative (I; R = Me, R′ = H), which was further methylated to the dimethyl derivative (I; R = R′ = Me) and benzoylated to the amine-amide (I; R = Me, R′ = Bz). A mixture of the mono- and di-



(I)



(II)



(III)

methyl derivatives was obtained from 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethylphenhomazine. The bathochromic shift and intensification of ultraviolet light absorption at longer wavelengths resulting from *N*-methylation of the base (I; R = R′ = H) are similar to the effects reported for the *N*-methylation of aniline.[5] Fission of the *endo*methylene bridge in the base (II; R = R′ = H) with toluene-*p*-sulphonyl chloride furnished a ditoluene-*p*-sulphonyl derivative (I; R = R′ = SO_2·C_6H_4Me-*p*) identical with that obtained directly from the disecondary base (I; R = R′ = H).

The formation of the 5 : 11-*endo*methylene bridge by treatment of the base (I;

* Part IV, *J.*, 1955, 991.

[1] Cooper and Partridge, *J.*, 1955, 991.
[2] Spielman, *J. Amer. Chem. Soc.*, 1935, **57**, 583.
[3] Cf. Jones and Kenner, *J.*, 1932, 711.
[4] Goecke, *Z. Elektrochem.*, 1903, **9**, 470.
[5] Ley and Specker, *Ber.*, 1939, **72**, 192.

R = R′ = H) with formaldehyde has been described previously.[1] The analogous 5 : 11-*endo*benzylidene derivative (II; R = H, R′ = Ph) was obtained in a similar manner with benzaldehyde, but the condensation was more efficient when water was removed azeotropically; its structure was confirmed by conversion into 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethyl-5 : 11-dinitrosophenhomazine (I; R = R′ = NO) and benzaldehyde on treatment with nitrous acid and by the similarity of its ultraviolet light absorption to that of Tröger's base.[1] The extension of this condensation to other aldehydes and to ketones is described in the Experimental section. Terephthalaldehyde afforded a bisphenhomazine, and *cyclo*hexanone a *spiro*-compound (II; RR′ = $-[CH_2]_5-$). Benzophenone did not undergo the condensation and no identifiable product was obtained from glucose or acetophenone. Tröger's base did not react with benzaldehyde under these conditions.

Attempts to introduce other types of 5 : 11-*endo*-bridge were less successful. A 5 : 11-*endo*ethoxymethylene derivative (II; R = H, R′ = OEt), which was rapidly converted into the dihydrochloride of the disecondary base (I; R = R′ = H) on treatment with hydrochloric acid, was formed from ethyl orthoformate. Although Tröger's base resulted from the dialkylation of the disecondary base (I; R = R′ = H) with methylene dibromide, reaction with tetramethylene or ethylene dibromide gave no recognisable product. Derivatives of carbonic acid did not lead to the 5 : 11-*endo*-carbonyl-bridged compound (II; RR′ = O). Diethyl carbonate could not be induced to react with the base (I; R = R′ = H) but diphenyl carbonate yielded the 5-phenoxycarbonylphenhomazine (I; R = CO_2Ph; R′ = H). In the presence of triethylamine, carbonyl chloride furnished the 5 : 11-di(chlorocarbonyl) derivative (I; R = R′ = COCl), which with ethanolic potassium hydroxide gave the ester (I; R = R′ = CO_2Et). This ester was also obtained together with the ester (I; R = CO_2Et, R′ = H) by interaction of the disecondary base (I; R = R′ = H) and ethyl chloroformate. With potassium cyanate in acetic acid or with molten urea the base (I; R = R′ = H) afforded the diurea (I; R = R′ = CO·NH_2), which gave the dinitroso-compound (I; R = R′ = NO) with nitrous acid. The corresponding substituted ureas (I; R = R′ = CO·NHPh, CS·NH_2, and CS·NHPh) were produced when phenyl *iso*cyanate, potassium thiocyanate, and phenyl *iso*thiocyanate respectively were brought into reaction with the disecondary base (I; R = R′ = H). Tröger's base did not react with potassium cyanate or with carbonyl chloride.

Ethyl oxalate failed to give any recognisable product but ethyl malonate gave the diacylated base (I; R = R′ = CO·CH_2·CO_2Et).

The interaction of 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethylphenhomazine with diazonium salts was also examined. In weakly acid solution, the colourless, bisdiazoamino-compounds (III; R = Ph, C_6H_4Me-*p* or C_6H_4Cl-*p*) were obtained. In agreement with this structure the phenylazo- and *p*-chlorophenylazo-derivatives (III; R = Ph or C_6H_4Cl-*p*) furnished the diacetylphenhomazine (I; R = R′ = Ac) on acetylation. Colourless diazoamino-compounds have previously been described by, *inter al.*, Henry and Dehn [6] and Wallach.[7]

Certain compounds described in this communication, particularly Tröger's base and its 5 : 11-*endo*vanillylidene and *p*-hydroxybenzylidene analogues, showed slight antibacterial and antifungal activity. None showed antiprotozoal or antiviral activity.

Experimental

5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethylphenhomazine* (I; R = R′ = H).—(*a*) A mixture of 40% formaldehyde solution (350 ml.) and concentrated hydrochloric acid (300 ml.) was slowly added to a cooled solution of *p*-toluidine (100 g.) in ethanol (1 l.). After 2 days, the solution

[6] Henry and Dehn, *J. Amer. Chem. Soc.*, 1943, **65**, 479.
[7] Wallach, *Annalen*, 1886, **235**, 233.

was concentrated to *ca.* 600 ml., basified with 33% aqueous ammonia (250 ml.), and distilled in steam to remove volatile bases. Sodium nitrite (85 g.) in water (3 l.) was added during 45 min. to a cooled solution of the residual base (104 g.) in a mixture of ethanol (400 ml.) and concentrated hydrochloric acid (200 ml.) and stirring was continued for 3 hr. The crude precipitated dinitroso-compound [60 g.; m. p. 230—232° (decomp.)], suspended in hot glacial acetic acid (500 ml.), was treated during 20 min. with a solution of cuprous chloride (45 g.) in concentrated hydrochloric acid (120 ml.) and expulsion of nitric oxide was completed by refluxing for 5 min. After removal of the solvent *in vacuo*, the residue was thoroughly triturated with 10% aqueous ammonia (1 l.), and the crude base (48 g.; m. p. 171—174°) was crystallised from benzene (charcoal) (yield 35·1 g., 32% overall; m. p. and mixed m. p. 204—205° [1]). Its *dihydrochloride* crystallised from 2N-hydrochloric acid as prisms, m. p. 289—290° (decomp.) when heated slowly from 200° (Found: C, 62·1; H, 6·4. $C_{16}H_{20}N_2Cl_2$ requires C, 61·7; H, 6·5%). The 5 : 11-*diformyl derivative*, obtained in 91% yield by 30 minutes' refluxing with excess of formic acid, crystallised from xylene as rods, m. p. 292—293° (Found: C, 73·4; H, 5·9. $C_{18}H_{18}O_2N_2$ requires C, 73·45; H, 6·15%).

(*b*) From the pure dinitroso-compound the yield was 83%; denitrosation in concentrated hydrochloric acid [3] gave only 10% of the desired product.

5 : 6 : 11 : 12-*Tetrahydro*-2 : 5 : 8-*trimethylphenhomazine* (I; R = Me; R′ = H).—Tröger's base (10 g.) and methyl sulphate (17 ml.) were shaken together in 2N-sodium hydroxide (200 ml.) for 1 hr. The insoluble material furnished the pure *trimethylphenhomazine* (7·9 g., 78%) as prisms, m. p. 147—148°, on crystallisation from light petroleum (b. p. 100—120°) (Found: C,80·6; H, 8·4; N, 11·0. $C_{17}H_{20}N_2$ requires C, 80·9; H, 8·0; N, 11·1%). Light absorption in EtOH: $\lambda_{max.}$ 208, 251, 301 mμ (ε 45,100, 18,100, 4000). Its *monopicrate*, prepared from the base and sodium picrate in aqueous lactic acid, crystallised from ethanol as prisms, m. p. 168—169° (Found: C, 57·5; H, 4·7; N, 14·5. $C_{23}H_{23}O_7N_5$ requires C, 57·35; H, 4·8; N, 14·55%). On benzoylation it yielded its 11-*benzoyl derivative* which crystallised from light petroleum (b. p. 100—120°) as prisms, m. p. 131—132° (Found: C, 80·5; H, 7·0; N, 7·6. $C_{24}H_{24}ON_2$ requires C, 80·9; H, 6·8; N, 7·85%).

5 : 6 : 11 : 12-*Tetrahydro*-2 : 5 : 8 : 11-*tetramethylphenhomazine* (I; R = R′ = Me).—(*a*) The product obtained by shaking the foregoing trimethyl derivative (1 g.) with methyl sulphate (1·5 ml.) in 2N-sodium hydroxide (25 ml.), when fractionally crystallised from light petroleum (b. p. 100—120°), furnished unchanged starting material (0·7 g.), m. p. and mixed m. p. 147—148°, and the *tetramethylphenhomazine* (0·05 g.), m. p. 149—150°, depressed to 125—131° by starting material (Found: C, 81·0; H, 8·1; N, 10·4. $C_{18}H_{22}N_2$ requires C, 81·15; H, 8·35; N, 10·5%). Light absorption in EtOH: $\lambda_{max.}$ 209, 261, 307 mμ (ε 41,500, 24,400, 4900). Attempted benzoylation of this compound afforded only unchanged starting material.

(*b*) 5 : 6 : 11 : 12-Tetrahydro-2 : 8-dimethylphenhomazine (3 g.) was methylated in a similar manner. Acid-soluble material (1·65 g.) was separated from the unchanged compound (1·15 g.) and was fractionally crystallised from light petroleum (b. p. 100—120°), furnishing the trimethylphenhomazine (0·3 g.) and the tetramethylphenhomazine (0·15 g.).

5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethyl*-5 : 11-*ditoluene*-p-*sulphonylphenhomazine* (I; R = R′ = $SO_2{\cdot}C_6H_4Me$-*p*) was obtained in 7% yield from Tröger's base and toluene-*p*-sulphonyl chloride under Schotten–Baumann conditions and crystallised from xylene as prisms, m. p. 270—271° (Found: C, 65·9; H, 5·6. $C_{30}H_{30}O_4N_2S_2$ requires C, 65·9; H, 5·55%).

5 : 6 : 11 : 12-Tetrahydro-2 : 8-dimethylphenhomazine acylated in pyridine gave the same compound, m. p. and mixed m. p. 270—271°, in 57% yield.

Interaction of 5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethylphenhomazine with Aldehydes and Ketones.*—A solution of the base (I; R = R′ = H) (2 g.) and the aldehyde or ketone (1—1·1 mols.) in benzene or xylene (80 ml.) was slowly distilled at atmospheric pressure and volatile material was finally removed at 100°/15 mm.; the residue was crystallised from a suitable solvent. Compounds so prepared are listed in the Table.

No. 1. With paraformaldehyde (4 mols., calc. as CH_2O) the solution was refluxed for 9 hr. before evaporation; m. p. and mixed m. p. with Tröger's base, 136—137°. The disecondary base (1 g.) and methylene bromide (6 ml.) when boiled together for 4 hr. gave Tröger's base in 33% yield but no identifiable product was isolated when the reagents were boiled in acetone in the presence of potassium carbonate.

No. 2. Excess of propionaldehyde was used as solvent.

No. 4. A solution of the base (1 g.) in benzaldehyde (4 ml.), concentrated hydrochloric

acid (5 ml.), and ethanol (20 ml.) was kept for 4 days and most of the solvent was removed. The insoluble material, after basification and recovery in ether, furnished the 5 : 11-endo-*benzylidene derivative*, m. p. and mixed m. p. 182—182°, in 33% yield [Found : *M* (Rast), 316. $C_{23}H_{22}N_2$ requires *M*, 326]. Light absorption in EtOH : $\lambda_{max.}$ 207, 237, 287 mμ (ε 40,300, 9300, 2300). This compound was soluble in dilute hydrochloric acid but not in dilute lactic acid. Its *monopicrate* crystallised from ethanol as small prisms, m. p. 205—206° (decomp.) (Found : C, 62·9; H, 4·9. $C_{29}H_{25}O_7N_5$ requires C, 62·7; H, 4·55%).

No. 6. The *monopicrate*, prisms from ethanol, had m. p. 195—196° (decomp.) (Found : C, 61·7; H, 4·95. $C_{30}H_{27}O_8N_5$ requires C, 61·55; H, 4·65%).

No. 8. This compound was soluble in aqueous sodium hydroxide but gave no ferric reaction.

No. 9. This compound was insoluble in aqueous sodium hydroxide and gave no ferric reaction.

No. 10. No reaction occurred in refluxing benzene.

No. 12. The product was purified by chromatography on alumina and occurred as a glass.

No. 14. The reagents were heated together at 183°; no reaction occurred in refluxing benzene. The *dipicrate* formed solvated prisms, m. p. 95—97° (effervescence), from benzene

TABLE 1. 5 : 11-endo-*Substituted*-5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazines*.

No.	5 : 11-*endo*-Substituent	Reaction solvent *	Solvent for crystn.†	Form
1	Methylene	B	Petrol	Needles
2	Propylidene	—	Petrol	Prisms
3	But-2-enylidene	B	EtOH	Prisms
4	Benzylidene	B	EtOH	Needles
5	Cinnamylidene	B	Petrol	Prisms
6	Anisylidene	B	Petrol	Prisms
7	*o*-Methoxybenzylidene	X	Petrol	Prisms
8	*p*-Hydroxybenzylidene	B	Petrol	Needles
9	Salicylylidene	X	Petrol	Prisms
10	Piperonylidene	X	Petrol	Prisms
11	Vanillylidene	X	MeOH	Needles
12	*p*-*n*-Pentyloxybenzylidene	B	—	—
13	*p*-Nitrobenzylidene	B	EtOH	Prisms
14	*p*-Dimethylaminobenzylidene	—	EtOH	Prisms
15	Furfurylidene	B	Petrol	Prisms
16	*iso*Propylidene	—	Petrol	Prisms
17	*cyclo*Hexylidene	—	Petrol	Prisms

				Found (%)			Required (%)		
No.	M. p.	Yield (%)	Formula	C	H	N	C	H	N
1	136—137°	95	—	—	—	—	—	—	—
2	80—81	52	$C_{19}H_{22}N_2$	81·7	7·85	10·2	81·95	7·95	10·05
3	121—122	84	$C_{20}H_{22}N_2$	82·7	7·55	9·65	82·7	7·65	9·65
4	182—183	95	$C_{23}H_{22}N_2$	84·6	6·7	8·75	84·6	6·8	8·6
5	142—143	97	$C_{25}H_{24}N_2$	85·2	7·15	8·05	85·2	6·85	7·95
6	155—156	95	$C_{24}H_{24}ON_2$	80·8	6·95	8·1	80·9	6·8	7·85
7	187—189	81	$C_{24}H_{24}ON_2$	80·9	6·65	7·65	80·9	6·8	7·85
8	220—221	97	$C_{23}H_{22}ON_2$	80·7	6·3	8·3	80·7	6·5	8·2
9	182·5—183·5	94	$C_{23}H_{22}ON_2$	81·0	6·2	7·95	80·7	6·5	8·2
10	160—161	87	$C_{24}H_{22}O_2N_2$	78·1	6·05	7·55	77·8	6·0	7·55
11	147—148	54	$C_{24}H_{24}O_2N_2$	77·3	6·45	7·75	77·4	6·5	7·5
12	—	61	$C_{28}H_{32}ON_2$	81·1	7·95	—	81·5	7·8	—
13	160·5—161	88	$C_{23}H_{21}O_2N_3$	73·9	6·0	11·1	74·35	5·7	11·3
14	178—179	91	$C_{25}H_{27}N_3$	81·0	6·95	11·3	81·25	7·35	11·35
15	135—135·5	92	$C_{21}H_{20}ON_2$	79·9	6·25	8·95	79·7	6·35	8·85
16	118—119	74	$C_{19}H_{22}N_2$	81·6	8·0	10·2	81·95	7·95	10·05
17	195—196	60	$C_{22}H_{26}N_2$	82·9	8·1	8·7	82·95	8·25	8·8

* B = benzene; X = xylene. † Petrol = light petroleum (b. p. 100—120°).

(Found : C, 60·2; H, 4·65; N, 12·4. $C_{37}H_{33}O_{14}N_9,2C_6H_6$ requires C, 59·8; H, 4·6; N, 12·8%).

No. 16. The reaction was carried out in excess of acetone and refluxing was for 6 hr. before evaporation.

No. 17. The reaction was carried out in excess of *cyclo*hexanone.

5 : 11-endo*Terephthalylidenebis*-(5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazine*), prepared in 79% yield by interaction of the tetrahydrophenhomazine and terephthalaldehyde in xylene, crystallised from xylene as prisms, m. p. 344—346° (decomp.) (Found : C, 83·7; H, 6·6; N, 9·7. $C_{40}H_{38}N_4$ requires C, 83·6; H, 6·65; N, 9·75%).

5 : 11-endo*Ethoxymethylene*-5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazine* (II; R = H; R′ = OEt) was produced (1·5 g., 61%) when the tetrahydrophenhomazine (2 g.) and ethyl orthoformate (10 ml.) were boiled together for 2 hr. and volatile material was removed at 100°/15 mm. After crystallisation of the residual glass first from light petroleum (b. p. 100—120°) and then from ethanol it formed colourless prisms, m. p. 114—116° (Found : C, 77·8; H, 7·55; N, 9·55. $C_{19}H_{22}ON_2$ requires C, 77·5; H, 7·55; N, 9·5%). Light absorption in EtOH : $\lambda_{max.}$ 209, 238, 284 mμ (ε 22,900, 8400, 2100). This compound slowly dissolved in 4N-hydrochloric acid, and the solution deposited 5 : 6 : 11 : 12-tetrahydro-2 : 8-dimethylphenhomazine dihydrochloride, identified by m. p. and mixed m. p. both of itself and of the base.

5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethylphenhomazine and Carbonic Acid Derivatives*.—(*a*) An ether solution of the clear melt which was obtained when the phenhomazine (2 g.) and phenyl carbonate (2 g.) were heated together at 182° for 3½ hr. was shaken with alkali and then with acid. The precipitate when crystallised from ethanol and then from light petroleum (b. p. 100—120°) gave the 5-*phenoxycarbonyl derivative* (I; R = CO_2Ph, R′ = H) (0·1 g.) as needles, m. p. 153—154° (Found : C, 77·3; H, 6·0; N, 8·0. $C_{23}H_{22}O_2N_2$ requires C, 77·05; H, 6·2; N, 7·8%).

(*b*) Carbonyl chloride in toluene (12·5%; 35 ml.) and dry, freshly distilled triethylamine (10 ml.) were added to the phenhomazine (4 g.) in toluene (100 ml.). After 2 hr., the suspension was basified with dilute aqueous ammonia, and the insoluble solid yielded the 5 : 11-*di*-(*chlorocarbonyl*) *derivative* (I; R = R′ = COCl) (4·15 g., 68%), m. p. 252·5—253°, as prisms on crystallisation from benzene (Found : C, 59·4; H, 4·5; N, 7·75. $C_{18}H_{16}O_2N_2Cl_2$ requires C, 59·55; H, 4·45; N, 7·7%). In the absence of triethylamine or when an old sample was used, the yield was greatly reduced.

(*c*) A mixture of the phenhomazine (1·5 g.), triethylamine (2·2 ml.), ethyl chloroformate (1·5 ml.), and benzene (20 ml.) was boiled for 30 min. and evaporated to dryness. The residue, after being washed with water, afforded, on fractional crystallisation from light petroleum (b. p. 100—120°), unchanged starting material (0·2 g.), the 5-*ethoxycarbonyl compound* (I; R = CO_2Et, R′ = H) (0·15 g.) as prisms, m. p. 117—118° (Found : C, 73·6; H, 7·15; N, 9·2. $C_{19}H_{22}O_2N_2$ requires C, 73·5; H, 7·15; N, 9·0%), and the 5 : 11-*di*(*ethoxycarbonyl*) *derivative* (I; R = R′ = CO_2Et) (0·45 g.) as prisms, m. p. 198—199° (Found : C, 69·4; H, 6·75; N, 7·3. $C_{22}H_{26}O_4N_2$ requires C, 69·1; H, 6·85; N, 7·35%). The last compound was also produced (54%) when the foregoing 5 : 11-di(chlorocarbonyl) derivative was boiled with aqueous-ethanolic potassium hydroxide for 1 hr.

5 : 11-*Dicarbamoyl*-5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazine* (I; R = R′ = $CO{\cdot}NH_2$) crystallised (1·7 g., 63%) when the tetrahydrophenhomazine (2 g.) and potassium cyanate (1·5 g.) were boiled together in glacial acetic acid (15 ml.) for 10 min.; it formed needles, m. p. 293—293·5°, after drying at 100° (Found : Loss at 150°/vac., 27·0. Found, on dried material : C, 66·6; H, 6·2; N, 17·0. $C_{18}H_{20}O_2N_4,2CH_3{\cdot}CO_2H$ requires $CH_3{\cdot}CO_2H$, 27·0. $C_{18}H_{20}O_2N_4$ requires C, 66·65; H, 6·2; N, 17·25%). The foregoing compound (0·6 g.), when treated overnight with sodium nitrite (1·2 g.) in aqueous acetic acid, furnished the corresponding 5 : 11-dinitroso-derivative (0·1 g.), m. p. and mixed m. p. 246—247°, together with unchanged starting material.

Although the mixture never became homogeneous when the tetrahydrophenhomazine (2 g.) and urea (10 g.) were heated together for 3 hr. at 155°, the water-insoluble fraction of the melt gave the 5 : 11-dicarbamoyl derivative (2·2 g., 81%), m. p. and mixed m. p. 292—293°.

5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethyl*-5 : 11-*di*(*thiocarbamoyl*)*phenhomazine*, prepared in a similar manner from potassium thiocyanate, crystallised from butan-1-ol as yellow prisms, m. p. 245—250° (decomp.) (Found : C, 61·0; H, 5·85; N, 15·4. $C_{18}H_{20}N_4S_2$ requires C, 60·65; H, 5·65; N, 15·7%).

5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethyl*-5 : 11-*di*(*phenylcarbamoyl*)*phenhomazine* (I; R = R′ = CO·NHPh), obtained (1·9 g., 95%) by interaction of phenyl *iso*cyanate (1·3 g.) and the phenhomazine (1 g.) in benzene (40 ml.), crystallised from xylene as prisms, m. p. 254—255° [Found : C, 76·0; H, 5·85; N, 11·8%; *M* (Rast), 462. $C_{30}H_{28}O_2N_4$ requires C, 75·6; H, 5·9; N, 11·75%; *M*, 477].

The corresponding 5 : 11-*di*(*phenylthiocarbamoyl*) *derivative*, prepared in an analogous manner, crystallised from benzene as prisms, m. p. 217—218° (Found : Loss at 140°/vac., 23·9. Found, on dried material : C, 70·8; H, 5·4; N, 11·0. $C_{30}H_{28}N_4S_2,2C_6H_6$ requires C_6H_6, 23·5. $C_{30}H_{28}N_4S_2$ requires C, 70·85; H, 5·55; N, 11·0%).

5 : 11-*Di*(*ethoxycarbonylacetyl*)-5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazine* (I; R = R′ = $CO{\cdot}CH_2{\cdot}CO_2Et$) was formed in 39% yield by boiling the phenhomazine (2 g.) with ethyl malonate (10 ml.) for 90 min., removing the volatile material at 160°/15 mm., and crystallising the residue from ethanol; it formed prisms, m. p. 149—149·5° (Found : C, 66·8; H, 6·55; N, 6·05. $C_{26}H_{30}O_6N_2$ requires C, 66·95; H, 6·5; N, 6·0%). No reaction occurred in refluxing benzene.

Interaction of 5 : 6 : 11 : 12-*Tetrahydro*-2 : 8-*dimethylphenhomazine and Diazonium Salts.*—(*a*) There was an immediate precipitate when aniline (1·2 g.), diazotised in hydrochloric acid, was added to a solution of the phenhomazine (1·5 g.) in dilute hydrochloric acid followed by sodium acetate (16·5 g.) and water. On crystallisation from benzene, the precipitate gave the 5 : 11-*di*(*phenylazo*)-*derivative* (1·7 g., 60%) as needles, m. p. 219—220° (decomp.) (Found : C, 75·6; H, 5·85; N, 18·7. $C_{28}H_{26}N_6$ requires C, 75·3; H, 5·85; N, 18·8%). Light absorption in hexane : $\lambda_{max.}$ 207, 240 mμ (ε 36,200, 17,200). On being boiled with acetic anhydride in glacial acetic acid, this compound gave the corresponding 5 : 11-diacetyl derivative (97%), m. p. and mixed m. p. 289—201° (Found : N, 8·4. Calc. for $C_{20}H_{22}O_2N_2$: N, 8·7%).

(*b*) 5 : 11-*Di*-(p-*chlorophenylazo*)-5 : 6 : 11 : 12-*tetrahydro*-2 : 8-*dimethylphenhomazine* crystallised from benzene as needles, m. p. 234—235° (decomp.) (Found : C, 65·2; H, 4·95; N, 16·0. $C_{28}H_{24}N_6Cl_2$ requires C, 65·25; H, 4·7; N, 16·3%), and furnished the same 5 : 11-diacetyl compound on acetylation.

(*c*) The 5 : 11-*di*-(p-*tolylazo*)*phenhomazine* occurred as colourless rods, m. p. 218—219° (decomp.), from benzene–light petroleum (b. p. 80—100°) (Found : C, 75·95; H, 6·7; N, 17·6. $C_{30}H_{30}N_6$ requires C, 75·95; H, 6·35; N, 17·7%).

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THE UNIVERSITY, NOTTINGHAM. [*Received, February 1st*, 1957.]