Investigations into the Mechanism of the Action of Alkali in Methanol on 3,6-Dibenzyl-*s*-tetrazines and their 1,4-Dihydro-derivatives: the Role of *s*-Tetrazines as Hydride Acceptors and an *X*-Ray Determination of the Structure of 3,6-Bis(4-chlorobenzyl)-1,4-dihydro-*s*-tetrazine

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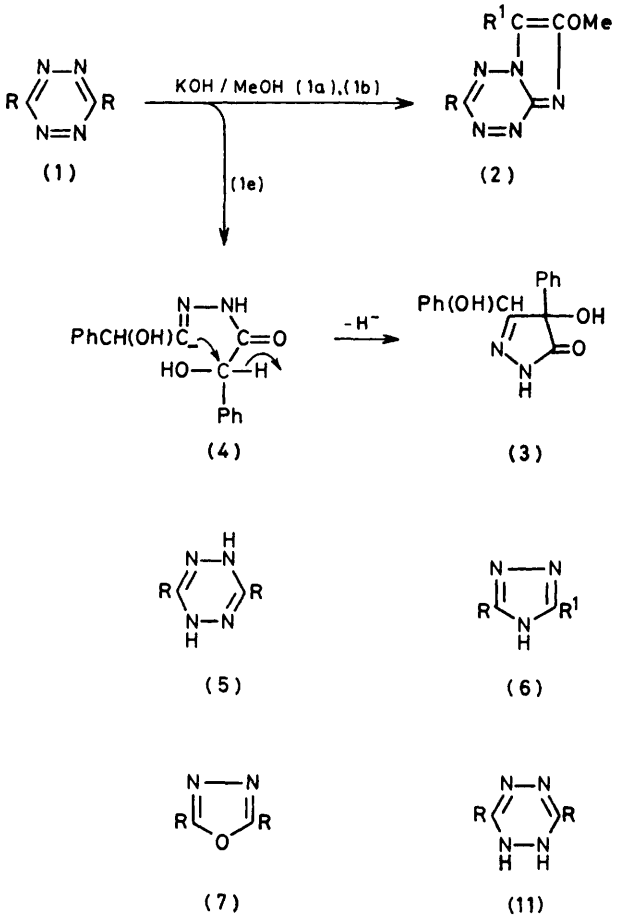
Evidence is presented for the mechanism of the reaction of potassium hydroxide with 3,6-dibenzyl-*s*-tetrazines in which some tetrazine molecules act as hydride acceptors to become dihydro-derivatives which, in turn, react with alkali in a competing reaction to form the corresponding 1,3,4-oxadiazoles. The known action of alkali on 3,6-dibenzyl-1,4-dihydro-*s*-tetrazines to form 1,3,4-oxadiazoles has been shown to require the presence of an oxidising agent and tetrazine can play this role. The structures of the dihydro-derivatives of *s*-tetrazines have been in doubt, being called 1,2- and/or 1,4-compounds almost at random, but an *X*-ray determination of the structure of the dihydro-derivative of 3,6-bis(4-chlorobenzyl)-*s*-tetrazine has shown conclusively that it exists as the 1,4-dihydro-compound.

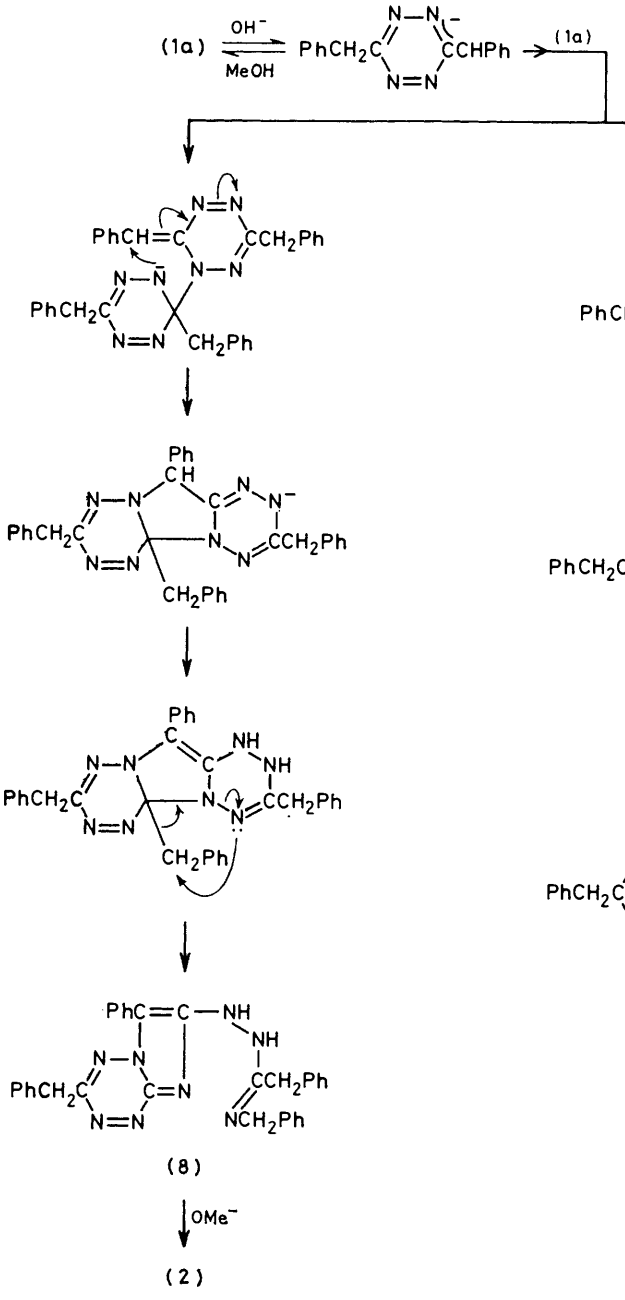
In recent papers,[1,2] the authors have shown that the effect of alkali in methanol on 3,6-symmetrically disubstituted *s*-tetrazines (1) depends markedly on the nature of the 3,6-substituents (1; R). Thus the tetrazines (1a) and (1b) form the corresponding imidazo-[1,2-*b*]-*s*-tetrazines [1] (2f,g) whereas 3,6-bis(α-hydroxybenzyl)-*s*-tetrazine (1e) yields a 4-hydroxy-3-(α-hydroxybenzyl)-4-phenylpyrazolin-5-one [2] (3) on treatment with alkali in methanol. In this latter process (1e) ⟶ (3) it was shown that the reaction proceeded *via* an intermediate of type (4) which ring-closed to give the pyrazolinone (3) by loss of a hydride ion which was accepted by a further molecule of the tetrazine (1e). This, in turn, picked up a proton to complete the reduction of the molecule of tetrazine (1e) to its dihydro-derivative.[2] Further studies have now been carried out on the effect of alkali on several 3,6-dibenzyl-*s*-tetrazines (1a—d) and their dihydro-derivatives (5) utilising this observation that *s*-tetrazines can act as redox reagents. This has permitted further insight into the mechanism of the reaction leading to the formation of species of the type (2).

(a) *Action of Alkali on* 3,6-*Dibenzyl*-s-*tetrazines*.—In addition to the compounds (1a,b) the novel tetrazines (1c,d) were prepared and treated with alkali as previously described,[1] but unfortunately the 3,6-bis(4-nitrobenzyl)-*s*-tetrazine (1d) did not yield any crystalline products on alkali treatment. In the other cases the yields of the corresponding imidazotetrazines (2f—h) increased as the electron-withdrawing effect at the 4-position of the benzyl group of the parent tetrazines (1a—c) was increased [*i.e.* in yield, (2h) < (2f) < (2g)]. This is in keeping with the proposed mechanism [1] (Scheme 1) involving proton removal from the benzylic methylene group as an initial step. The tetrazine (1c) on treatment, in air, with base in methanol for a briefer time than previously reported,[1] yielded, in addition to the expected imidazotetrazine (2h), new products *viz.* 3-(4-methoxybenzyl)-5-(4-methoxyphenyl)-1,2,4(4*H*)-triazole (6h), 2,5-bis(4-methoxybenzyl)-1,3,4-oxadiazole

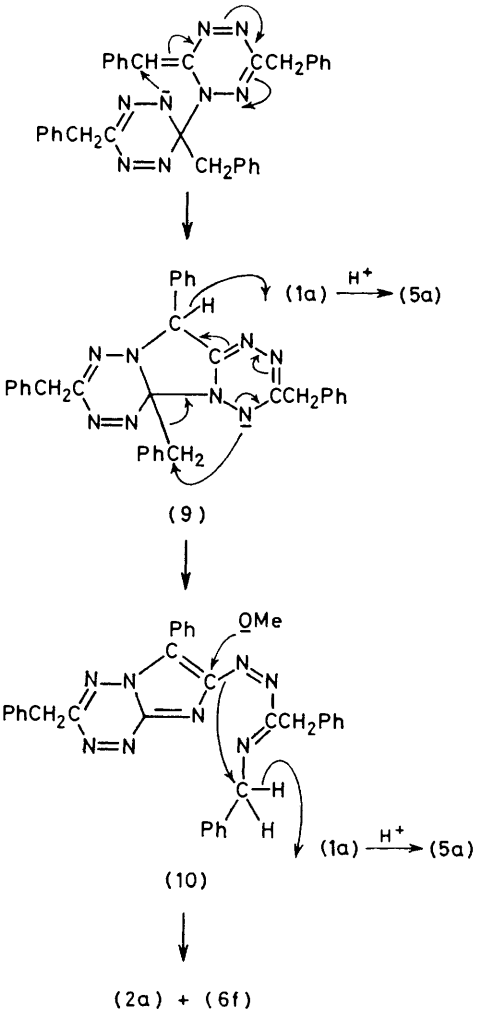


(1) (2) (4) (3) (5) (6) (7) (11)

a; R = $PhCH_2$
b; R = 4-$ClC_6H_4CH_2$
c; R = 4-$MeOC_6H_4CH_2$
d; R = 4-$O_2NC_6H_4CH_2$
e; R = PhCH(OH)
f; R = $PhCH_2$, R^1 = Ph
g; R = 4-$ClC_6H_4CH_2$, R^1 = 4-ClC_6H_4
h; R = 4-$MeOC_6H_4CH_2$, R^1 = 4-$MeOC_6H_4$



SCHEME 1



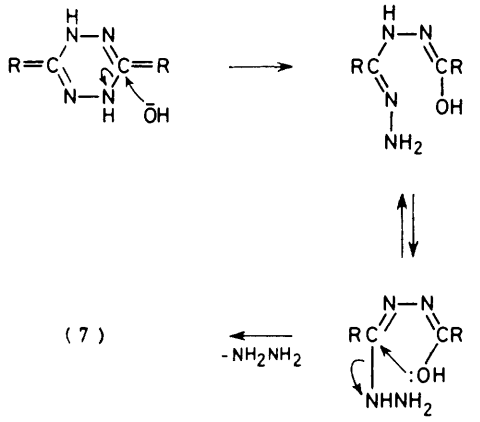
SCHEME 2

(7c), and the methyl esters of 4-methoxybenzoic and 4-methoxyphenylacetic acids. The identification of the triazole (6h) adds weight to the mechanism (Scheme 1) proposed in our earlier paper in which the triazole can be envisaged as arising from the side chain in precursor (8) by oxidative cyclisation following displacement by methoxide. Tetrazines, moreover, are not known to yield oxadiazoles except on treatment with peracids [3,4] and hence the oxadiazole (7) must arise from some other precursor. Dihydrotetrazines,* on the other hand, have been shown to give oxadiazoles on treatment with alkali [6] and, in addition, can readily reform tetrazines in the presence of air.[5] The absence of any dihydrotetrazine in the product mixture was not, therefore, surprising but suggested the necessity of repeating the experiments under nitrogen. When this was done the reaction mixture showed the presence of the previous products (2h),

* There is considerable confusion in the literature and no real certainty as to whether these dihydro-compounds are the 1,2- or 1,4-dihydro-*s*-tetrazines.[5] Conflicting evidence has been presented for both substitution patterns and the position is further complicated by the ' isomeric ' 4-amino-1,2,4-triazoles, which often simultaneously occur in preparations, being mistaken in earlier work for the dihydrotetrazines. See section (b) for a fuller discussion.

(6h), and (7c), and, in addition, some dihydrotetrazine (5c); this confirmed a potential source of the oxadiazole (7c).

The presence of the dihydrotetrazine (5c) also permits a modified reaction mechanism, involving tetrazine as a hydride ion acceptor (Scheme 2), to be proposed for the formation of the imidazotetrazine (2h). In this the driving force for the 1,3-benzyl shift [see intermediate (9)] is not only the aromatisation of the imidazotetrazine moiety but also the removal of a negative charge on nitrogen. The side chain of the proposed intermediate (10) is then set up for displacement by methoxide ion, with the subsequent aromatisation of the fragment to the unsymmetrically 3,5-disubstituted 1,2,4-triazole (6) occurring by loss of hydride ion from the benzylic methylene to a further molecule of tetrazine.

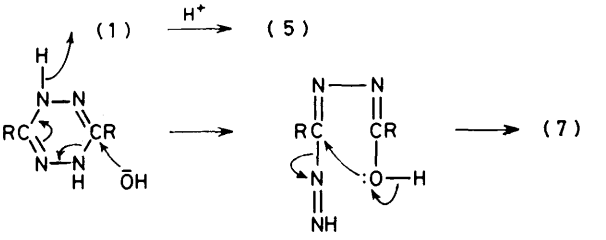


SCHEME 3

A related series of products was obtained when the action of alkali on the tetrazine (1b) was reinvestigated, under conditions identical with those above, and the unsymmetrically substituted triazole (6f) was isolated from the tetrazine (1a).

(b) *Action of Alkali on* 3,6-*Dibenzyl*-1,4-*dihydro*-s-*tetrazines*.—There has been considerable confusion in the literature over the exact identity of many dihydrotetrazines (see earlier footnote). In section (c) of this paper, evidence will be presented which shows that compound (5b) has in fact, in the solid phase at least, a 1,4-dihydro-structure. This result supports evidence from other workers [7] who came to the conclusion that the 1,4-dihydro-substitution pattern was to be preferred over the 1,2-dihydro-arrangement on the basis of alkylation reactions and spectral comparisons. However, it was admitted by these authors [7] that their results were not absolutely conclusive.

When a methanolic solution of potassium hydroxide was added to the 1,4-dihydrotetrazine (5b), in contact with air, the main product was 2,5-bis(4-chlorobenzyl)-1,3,4-oxadiazole (7b) confirming earlier related work in the literature.[6] However, when the experiment was carried out under nitrogen (but in an otherwise analogous manner) no oxadiazole (7b) was isolated and the dihydrotetrazine (5b) was to a large extent recovered unchanged. Analogous results were found for the 4-methoxybenzyl system (5c) ⟶ (7c) and this suggests that the simple hydrolysis mechanism for the formation of oxadiazole (Scheme 3) may not hold and illustrates that, in fact, the presence of an oxidising agent (*e.g.* air) is required for oxadiazole formation. Having shown that tetrazines have the ability to act as oxidising agents [2] (see



SCHEME 4

also above) the experiment was repeated utilising a mixture of the 1,4-dihydrotetrazine (5b) and the tetrazine (1b) in contact with alkali in methanol under nitrogen. Competing reactions (1b) ⟶ (2g) and (5b) ⟶ (7b) took place but the oxadiazole (7b) was conclusively identified as occurring in the product mixture to a much greater extent (×8) than would be expected on the basis of the tetrazine decomposition (1b) ⟶ (2g), (6g), and (7b) alone thus confirming the role of tetrazine as an oxidant. Hence it is proposed that the mechanism for the formation of the oxadiazole (7) from the 1,4-dihydrotetrazine (5) is as shown in Scheme 4 and involves an oxidation step with transfer of a hydride ion to the tetrazine.

(c) *Structure of* 3,6-*Bis*(4-*chlorobenzyl*)-1,4-*dihydro*-s-*tetrazine* (5b).—An *X*-ray structure investigation of the dihydrotetrazine (5b) showed the molecule to be partly disordered. The chlorophenyl groups appear fixed but the N(2) atom lies at two sites N(2A) and N(2B) with refined site occupancy factors 0.505 (14) and 0.495 (14) respectively (Figure). The methylene atom C(7) and the atoms C(8) and N(1) of the central dihydrotetrazine ring have high anisotropic thermal parameters although alternate sites for these atoms could not be distinguished. Evidence from the bond lengths shows that the compound is without doubt the 1,4-derivative and not a 1,2-isomer. The C(8)–N(1) bond is double (1.27 Å) while the other bonds in the heterocyclic ring are single. Attempts to model the compound as the 1,2-dihydro-isomer resulted in abnormal bond lengths and such models assuming the presence of acentric molecules derived from 1,2-dihydrotetrazine (11b), with or without static disorder, failed to refine satisfactorily.

An acceptable interpretation of the data, consistent with the atomic positions and site occupancy factors, is that the disorder involves two 1,4-dihydrotetrazine moieties each occurring in an acentric boat conformation with equal probability, *i.e.* atoms C(8), N(1), N(2A'), C(8'), N(1'), and N(2B) and the crystallographic centrosymmetrically related set. In this model the

double bond C(8)–N(1) and the two adjacent bonds [C(8)–N(2B) and N(1)–N(2A')] are almost coplanar and the intermolecular distances N(1) · · · N(2A) (2.97 Å) and N(1) · · · N(2B) (2.99 Å) are consistent with N–H · · · N hydrogen bonds.

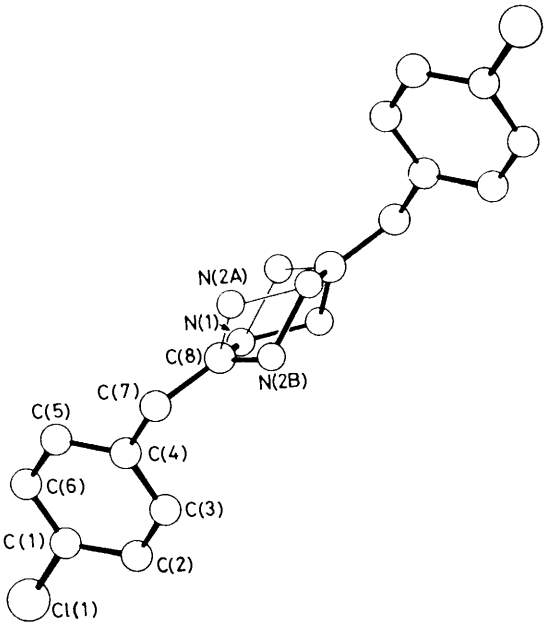


FIGURE Alternative conformations of the dihydrotetrazine ring in $C_{16}H_{14}Cl_2N_4$ (*b* axis projection)

EXPERIMENTAL

Preparation of Imidate Salts.—Using standard Pinner [8,9] syntheses the following imidate salts were prepared from the corresponding nitriles: ethyl phenylacetimidate hydrochloride (65%), m.p. 100—102 °C (decomp.) [lit.,[10] 99—100 °C (decomp.)]; ethyl 4-chlorophenylacetimidate hydrochloride (73%), m.p. 180—183 °C after shrinkage and decomp. at 130 °C [lit.,[11] 130 °C (decomp.)]; ethyl 4-methoxyphenylacetimidate hydrochloride (68%), m.p. 103—106 °C (decomp.); and ethyl 4-nitrophenylacetimidate hydrochloride * (96%), m.p. 194—198 °C after decomposition at 122 °C (lit.,[11] m.p. 195 °C).

Preparation of the Tetrazines (1).—The compounds (1a), (1b), (1c), and (1d) were prepared as previously described.[1] They had the following properties: 3,6-dibenzyl-*s*-tetrazine (1a), m.p. 73—75 °C (lit.,[12] 74 °C), yield 49% (from methanol); 3,6-bis(4-chlorobenzyl)-*s*-tetrazine (1b), m.p. 135—136 °C (lit.,[1] 135—137 °C), yield 43% (from methanol); 3,6-bis(4-methoxybenzyl)-*s*-tetrazine (1c), m.p. 122 °C (50%) (from ethanol) (Found: C, 66.4; H, 5.5; N, 17.4. $C_{18}H_{18}N_4O_2$ requires C, 67.1; H, 5.6; N, 17.4%); 3,6-bis(4-nitrobenzyl)-*s*-tetrazine (1d), m.p. 194—195 °C (49%) (from acetone) (Found: C, 54.2; H, 3.4; N, 23.9. $C_{16}H_{12}N_6O_4$ requires C, 54.5; H, 3.4; N, 23.9%).

Preparation of the 1,4-*Dihydrotetrazines* (5).—In a typical preparation sodium dithionite (6 g) was added in portions to a suspension of the tetrazine (1b) (2 g) in a methanol–water (80 ml; 3 : 1 v/v) mixture at room temperature with vigorous stirring. After 1 h the largely decolourised suspension was poured into water (200 ml) and the resultant solid was filtered off. The product obtained was 3,6-*bis*(4-*chlorobenzyl*)-1,4-*dihydro*-s-*tetrazine* (5b) (1.9 g), m.p. 203—204 °C (from ethyl acetate) (Found: C, 57.8; H, 4.2; N, 16.8. $C_{16}H_{14}Cl_2N_4$ requires C, 57.7; H, 4.2; N, 16.8%).

3,6-*Bis*(4-*methoxybenzyl*)-1,4-*dihydro*-s-*tetrazine* (5c), prepared similarly, had m.p. 204 °C (from ethyl acetate) (Found: M^+, 324.157 29. $C_{18}H_{20}N_4O_2$ requires M^+, 324.158 60).

Action of Methanolic Potassium Hydroxide on 3,6-*Bis*(4-*methoxybenzyl*)-s-*tetrazine* (1c).—(a) *In air.* A solution of potassium hydroxide (0.6 g) in methanol (9 ml) was added dropwise to a stirred suspension of the tetrazine (1c) (2.5 g) in methanol (19 ml). Stirring was continued for 4 h, by which time the tetrazine had dissolved, and the brown solution was set aside overnight. The volume was then decreased under reduced pressure by about half, water was added and the mixture extracted with ethyl acetate. The dried extract was separated on a dry column [13] [silica eluted first with diethyl ether–light petroleum (b.p. 40—60 °C) 3 : 2, and then with diethyl ether alone]. The forerun consisted of the methyl esters of *p*-methoxybenzoic (0.3 g) and *p*-methoxyphenylacetic acids (0.14 g), then an orange solid, and finally the unsymmetrically substituted triazole (6h), identical with a synthetic sample (see later). The orange solid was further separated chromatographically [13] (chloroform on silica) into 2,5-*bis*(4-*methoxybenzyl*)-1,3,4-*oxadiazole* (7c) (0.1 g), m.p. 76—77 °C [from toluene–light petroleum (b.p. 80—100 °C)] (Found: C, 69.7; H, 5.7; N, 8.9%. $C_{18}H_{18}N_2O_3$ requires C, 69.7; H, 5.8; N, 9.0%), and 7-*methoxy*-3-(4-*methoxybenzyl*)-6-(4-*methoxyphenyl*)*imidazo*-[1,2-b]-s-*tetrazine* (2h) (0.54 g), m.p. 179—180 °C (from acetone) (Found: C, 63.5; H, 4.9; N, 18.4. $C_{20}H_{19}N_5O_3$ requires C, 63.7; H, 5.0; N, 18.6%).

(b) *Under nitrogen.* The experiment was repeated on one-fifth of the scale but under nitrogen and the reaction mixture quenched with acid on opening to air. T.l.c. examination of the dried ethyl acetate extract demonstrated the presence of the tetrazine (1c), the imidazotetrazine (2h), the triazole (6h), the oxadiazole (7c), and the dihydrotetrazine (5c) which, on exposure to air on the t.l.c. plate, gradually oxidised to the red tetrazine (1c) showing unequivocally the presence of compound (5c).

Repetition of the experiment in air but utilising the chloro-substituted tetrazine (1b) (4 g) led similarly, by the chromatographic elution [13] [ethyl acetate–light petroleum (b.p. 40—60 °C) 2 : 3 on silica] of the solid obtained directly from the reaction mixture, to 3-(4-chlorobenzyl)-6-(4-chlorophenyl)-7-methoxyimidazo[1,2-*b*]-*s*-tetrazine (2g) (1.4 g), identical with a previously prepared sample.[1] The extract of the reaction liquors gave, on chromatographic separation [13] [diethyl ether–light petroleum (b.p. 40—60 °C) 1 : 1 on silica], a little of the same compound (2g) as well as the triazole (6g) (0.56 g) and the oxadiazole (7b) (0.07 g) both of which were identical with authentic samples (see later).

Under identical experimental conditions 1M-portions of each of the tetrazines (1a), (1b), and (1c) gave the imidazotetrazines (2f), (2g), and (2h) in the molar ratios 0.21 : 0.30 : 0.12, respectively.

The action of potassium hydroxide in methanol on the nitro-substituted *s*-tetrazine (1d) under conditions related to the above gave no useful products.

Action of Methanolic Potassium Hydroxide on 1,4-*Dihydrotetrazines* (5).—(a) *In air.* A solution of potassium hydroxide (0.5 g) in methanol (6 ml) was added dropwise with stirring to the dihydrotetrazine (5b) (1.4 g) in methanol (12 ml) at room temperature. The solution became red

* Nitrobenzene was used as diluent in this case.

after a few drops of the base were added. Stirring was continued for 2 h. After standing overnight the volume of the solution was decreased under reduced pressure by *ca.* one-half and the residue poured into water and extracted with ethyl acetate. Chromatographic separation [13] [diethyl ether–light petroleum (b.p. 40—60 °C) 1 : 1 on silica] yielded a trace of the imidazotetrazine (2g) but mainly the *oxadiazole* (7b) (0.5 g), m.p. 78—79 °C [from toluene–light petroleum (b.p. 80—100 °C)] (Found: M^+, 318.032 41. $C_{16}H_{12}Cl_2N_2O$ requires M^+, 318.032 65).

(b) *Under nitrogen.* Repetition of the above experiment under nitrogen, but otherwise using an analogous procedure, did not give a red colour and the starting material (5b) was recovered in 84% yield.

Analogous results to both the above were obtained when the dihydrotetrazine (5c) was used, *i.e.* in air the oxadiazole (7c) was identified and under nitrogen the starting material was recovered in 81% yield.

(c) *Under nitrogen in the presence of the parent tetrazine* (1b). A solution of potassium hydroxide (0.5 g) in methanol (6 ml) was added dropwise with stirring to a mixture of the dihydrotetrazine (5b) (0.45 g) and the tetrazine (1b) (0.45 g) in methanol (12 ml) at room temperature under nitrogen. After the mixture had been set aside overnight the solid material was filtered off and the filtrate quenched with dilute hydrochloric acid. The solid material yielded, on chromatographic separation [13] (diethyl ether on silica), the dihydrotetrazine (5b) (0.19 g) and the imidazotetrazine (2g) (0.15 g). An ethyl acetate extract of the quenched filtrate yielded, on chromatographic separation [13] [diethyl ether–light petroleum (b.p. 40—60 °C) 1 : 1 on silica] the tetrazine (1b) (0.08 g), the imidazotetrazine (2g) (0.15 g), the triazole (6g) (0.23 g), and the oxadiazole (7b) (0.07 g). The two last named compounds ran together and could not be separated chromatographically but their proportions were calculated from the n.m.r. spectra of the mixture and by comparison with ' synthetic ' mixtures. [On the basis of all the tetrazine (1b) having changed the maximum yield of oxadiazole (7b) arising from that source would be *ca.* 8 mg, *i.e.* about one-ninth of the total actual yield, and hence the greater bulk of this material (7b) must have arisen from the dihydrotetrazine (5b).]

Preparation of Unsymmetrically 3,5-Disubstituted 1,2,4-Triazoles (6).—The following triazoles were prepared by the action of the appropriate imidate and acyl hydrazide following published procedures: [14] 3-benzyl-5-phenyl-1,2,4-(4*H*)-triazole (6f), softened 113—114 °C, m.p. 126—128 °C (from aqueous ethanol) (lit.,[14] 113—114 °C). The fusion characteristics of this compound were variable, the lower m.p. sometimes being observed (Found: C, 76.8; H, 5.7; N, 18.0. $C_{15}H_{13}N_3$ requires C, 76.6; H, 5.5; N, 17.9%); 3-(4-*chlorobenzyl*)-5-(4-*chlorophenyl*)-1,2,4(4H)-*triazole* (6g) had m.p. 155—157 °C (from aqueous ethanol) (Found: C, 58.7; H, 3.6; N, 13.7. $C_{15}H_{11}Cl_2N_3$ requires C, 59.2: H, 3.6; N, 13.8%); 3-(4-*methoxybenzyl*)-5-(4-*methoxyphenyl*)-1,2,4(4H)-*triazole* (6h) had m.p. 164—165 °C (from aqueous ethanol) (Found: C, 69.3; H, 5.8; N, 14.4. $C_{17}H_{17}N_3O_2$ requires C, 69.2; H, 5.8; N, 14.2%).

These compounds (6f), (6g), and (6h) were identical with samples isolated from tetrazines by the action of alkali (see earlier).

Preparation of Oxadiazoles (7).—These were prepared by the action of peracetic acid [15] on the tetrazines (1b) and (1c) using published procedures.[3,4] 2,5-*Bis*(4-*chlorobenzyl*)-1,3,4-*oxadiazole* (7b) (27%), m.p. 78—79 °C [from toluene–light petroleum (b.p. 80—100 °C)] was identical in mixed m.p. and spectral detail with that obtained from the dihydrotetrazine (5b) (see above for analytical details). Similarly 2,5-*bis*(4-*methoxybenzyl*)-1,3,4-*oxadiazole* (7c) (22%), m.p. 75—76 °C [from toluene–light petroleum (b.p. 80—100 °C)] was identical with a sample (7c) from the dihydrotetrazine (see above).

X-*Ray Data.*—The crystals were colourless, air-stable prisms elongated along [010]. They became progressively deeper pink during irradiation but no sign of decomposition could be detected in diffraction photographs.

Crystal data.—$C_{16}H_{14}Cl_2N_4$, M = 333.2, monoclinic, space group, $P2_1/c$, a = 5.827(4), b = 5.132(3), c = 26.63(4) Å, β = 99.55(9)°, V = 786.7 Å^3, Z = 2, D_c = 1.407 g cm^{-3}, $F(000)$ = 344; Cu-$K\alpha$ radiation (λ = 1.5418 Å), μ = 35.8 cm^{-1}.

Multi-film equi-inclination Weissenberg photographs of the reciprocal lattice layers $h0$—$4l$ and 0—$5kl$ were scanned by use of a microdesitometer (S.R.C. Service, Daresbury Laboratory); 835 unique reflections were above background. Absorption corrections were applied during data reduction. Because of the short b axis the assignment of the space-group as $P2_1/c$ rather than $P2/c$ or the acentric Pc rested on the absence of only three reflections. Therefore the structure was initially solved in Pc by use of direct methods. For this purpose it was necessary to renormalize the $|E|$ values for odd l, or to include 880 unobserved reflections in the

TABLE 1

Atomic co-ordinates and equivalent isotropic thermal parameters (all × 10^4)

	x	*y*	*z*
Cl	1 222(2)	2 395(2)	2 927(1)
C(1)	2 979(7)	4 752(9)	3 260(2)
C(2)	2 469(8)	5 729(11)	3 717(2)
C(3)	3 888(10)	7 614(11)	3 973(2)
C(4)	5 778(8)	8 533(9)	3 792(2)
C(5)	6 308(9)	7 507(10)	3 346(2)
C(6)	4 912(8)	5 626(10)	3 077(2)
C(7)	7 233(10)	716(10)	4 061(2)
C(8)	8 639(9)	124(9)	4 560(2)
N(1)	9 133(8)	7 843(7)	4 727(1)
N(2A)	8 600(14)	2 182(13)	4 910(3)
N(2B)	355(16)	2 206(13)	4 712(3)
H(1) [a]	1 130	4 660	3 850
H(2) [a]	3 500	8 440	4 290
H(3) [a]	7 740	8 180	3 210
H(4) [a]	5 110	4 840	2 740

[a] Hydrogen parameters not refined.

TABLE 2

Interatomic distances (Å) and interbond angles (°)

Cl–C(1)	1.732(4)	C(4)–C(7)	1.512(6)
C(1)–C(2)	1.392(6)	C(7)–C(8)	1.473(6)
C(2)–C(3)	1.379(7)	C(8)–N(1)	1.268(6)
C(3)–C(4)	1.359(7)	C(8)–N(2A)	1.412(8)
C(4)–C(5)	1.381(7)	C(8)–N(2B)	1.475(8)
C(5)–C(6)	1.384(6)	N(1)–N(2A′)	1.504
C(1)–C(6)	1.376(6)	N(1)–N(2B′)	1.473
Cl–C(1)–C(2)	120.3(3)	C(4)–C(7)–C(8)	117.3(4)
Cl–C(1)–C(6)	119.8(3)	C(7)–C(8)–N(1)	124.6(4)
C(2)–C(1)–C(6)	119.9(4)	C(7)–C(8)–N(2A)	111.9(5)
C(1)–C(2)–C(3)	119.2(4)	C(7)–C(8)–N(2B)	110.5(4)
C(2)–C(3)–C(4)	121.6(4)	N(1)–C(8)–N(2A)	119.1(4)
C(3)–C(4)–C(5)	118.9(4)	N(1)–C(8)–N(2B)	117.9(5)
C(3)–C(4)–C(7)	121.0(5)	C(8)–N(1)–N(2A′)	111.0(6)
C(5)–C(4)–C(7)	120.0(5)	C(8)–N(1)–N(2B′)	111.5(6)
C(4)–C(5)–C(6)	120.9(4)	C(8)–N(2A)–N(1′)	108.0(6)
C(1)–C(6)–C(5)	119.5(4)	C(8)–N(2B)–N(1′)	106.4(6)
N(1) · · · N(2A)	2.971(11)	N(1) · · · N(2B)	2.981(11)

data set with $|F|$ set arbitrarily at $0.2\,|F_o|_{min.}$; in either case the E-maps then clearly showed the same molecular fragments (the Cl and all benzyl C atoms), with weaker indications of the other non-hydrogen atoms. The positions of the latter were confirmed in a difference synthesis following three cycles of full-matrix least-squares refinement (observed reflections only). A satisfactory further refinement was carried out in the centric space-group $P2_1/c$ with the assumption of disorder as described above. The four hydrogen atoms of the phenyl ring were located in a difference synthesis and were included with fixed parameters in the last cycles. Convergence was reached at R 0.060, R_w 0.065 (anisotropic thermal parameters for all Cl, C, and N atoms, 110 parameters, weighting factor $w = [1 + 0.0076F^2]^{-1}$). The *SHELX* 76 program was used in all calculations.[16] Atomic co-ordinates are detailed in Table 1 and interatomic distances and bond angles in Table 2. The structure factors and the anisotropic thermal parameters for this work are available as a Supplementary publication (Sup. No. 23239, 7 pages).*

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* For details of the Supplementary publications scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

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