Base-catalysed Ring Contraction of 6,7-Dihydro-1-methyl-1*H*-1,2,5-triazepines to 2,3-Dimethyl-1,2,4-triazines

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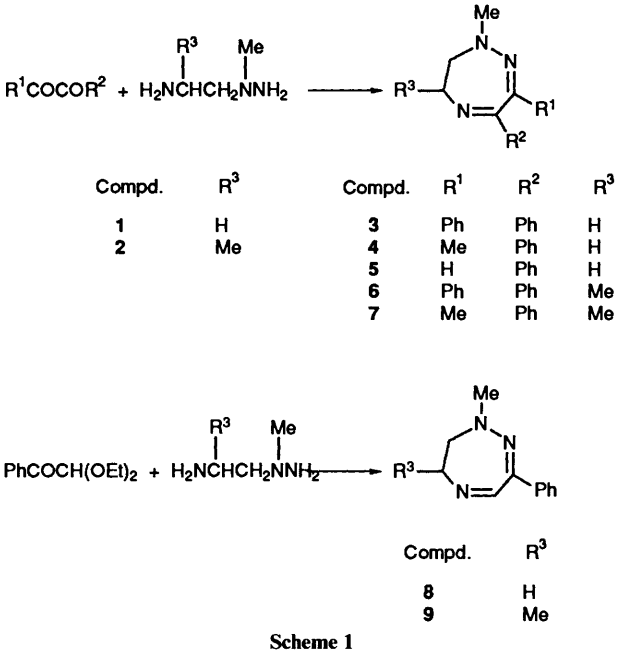
6,7-Dihydro-1-methyl-1*H*-1,2,5-triazepines **3–5** and **8** in ethanolic sodium hydroxide have been converted into one or two compounds of the following types: 1,2,3,6-tetrahydro-6-hydroxy-, 1,2-dihydro- and 2,3-dihydro-2,3-dimethyl-1,2,4-triazines **10–16**. In contrast, 1,6-dimethyl analogues are converted into the corresponding 2,3-dihydro-2,3,3-trimethyl-1,2,4-triazines **17–19** under similar conditions. Since alkali hydroxide is essential to the present ring contraction it is likely that it proceeds *via* a 3-hydroxylated anion formed by hydroxide attack on the 3-position of triazepines **3–9**. 1,2,3,6-Tetrahydro-6-hydroxy-2,3-dimethyl-1,2,4-triazines **10–12** are found to be precursors to the 1,2-dihydro-2,3-dimethyl-1,2,4-triazines **13–15**.

Of the four possible monocyclic triazepines, the 1,2,4-system has been most studied, the chemistry of the others having generated few reports on account of their lack of stability and unavailability.

In general, base-catalysed ring contraction of triazepines appears to proceed either through deprotonation followed by cleavage of an N–N bond[1] or *via* a diaziridine intermediate.[2] Thermal ring-contraction mechanisms have been reported to proceed *via* a diaziridine intermediate,[3] a triazanorcaradiene[4] or by a 1,3-sigmatropic rearrangement with nitrogen.[5] Here we report a novel ring contraction of 1,2,5-triazepines which is thought to proceed *via* a covalently hydroxylated intermediate under base-catalysed conditions.

Results and Discussion

In the preparation of 6,7-dihydro-1-methyl-1*H*-1,2,5-triazepines, the 3-methyl-4-phenyl compound **4** was prepared in a similar fashion to the 3,4-diphenyl compound **3**[6] from the reaction of 1-phenylpropane-1,2-dione with 1-(2-aminoethyl)-1-methylhydrazine **1**.[7] The 4-phenyl **5** and 3-phenyl compound **8** were prepared from phenylglyoxal monohydrate or phenylglyoxal diethyl acetal with **1** in chloroform, respectively. 6,7-Dihydro-1,6-dimethyl-1*H*-1,2,5-triazepines **6**, **7** and **9** were prepared from the reaction of 1,2-diketones with 1-(2-aminopropyl)-1-methylhydrazine **2**[7] in a similar way to the preparation of compounds **3**, **4** and **8** (Scheme 1).



Compd.	R^3
1	H
2	Me

Compd.	R^1	R^2	R^3
3	Ph	Ph	H
4	Me	Ph	H
5	H	Ph	H
6	Ph	Ph	Me
7	Me	Ph	Me

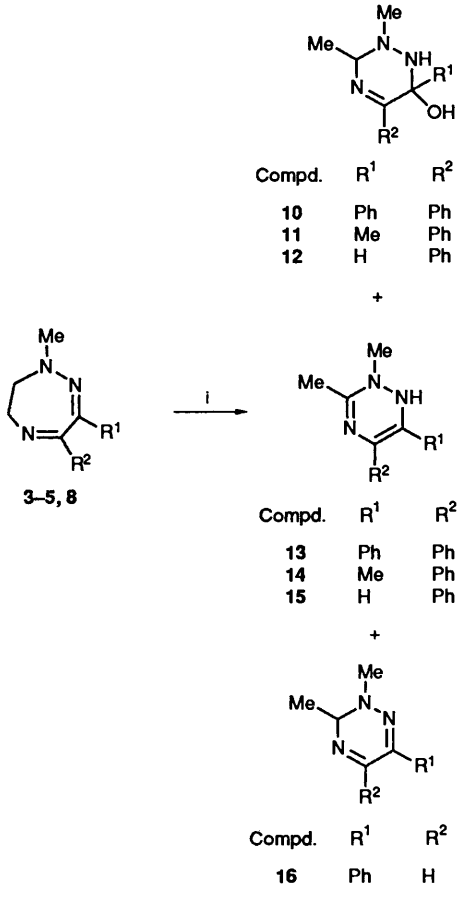
Compd.	R^3
8	H
9	Me

Scheme 1

The structures of the dihydrotriazepines **3–9** were established on the basis of their analytical and spectral results. Thus, the absence of OH, NH and C=O absorption indicated that compounds **3–9** had a cyclic rather than a linear structure. In their ^{1}H NMR spectra, the dihydrotriazepines **4**, **5** and **8** had signals at δ 3.8–3.65 and 3.69–4.14 (both 2 H, m), closely similar to the reported values for **3**.[6] The appearance of the multiplets strongly suggests the presence of four non-equivalent protons on adjacent methylene groups, 5-nitrogen adjacent to the 6-position being responsible for the downfield signal. The protons of the 4-phenyl **5** and 3-phenyl compound **8** showed multiplets at δ 7.38–7.65 and 7.41 respectively. The appearance of the phenyl protons as a multiplet suggests that the 4- and 3-carbons are sp^2-hybridized. Further support for the seven-membered ring structure comes from the Eu-induced shift experiments on compounds **5** and **8**. The magnitude of the chemical shifts brought about by the addition of a shift reagent [Eu(dpm)] clearly indicates that compound **8** involves an unhindered nitrogen.

Base-catalysed ring contraction of **3** was induced by heating it in refluxing 10% ethanolic sodium hydroxide for 2 h, chromatographic separation then giving 2,3-dimethyl-1,2,4-triazine derivatives **10** and **13**. Triethylamine failed to effect the reaction, resulting only in recovery of the starting triazepine. Other triazepines **4** and **5** were similarly converted into the corresponding triazines **11**, **12**, **14** and **15**. In contrast, the triazepine **8** isomeric with **5**, gave the corresponding 2,3-dihydro-2,3-dimethyl-1,2,4-triazine **16** as the sole product (Scheme 2). The time required for completion of the ring contraction was dependent on both the substitution pattern of the starting triazepines and the concentration of the hydroxide. In the 4-phenyl series, **3–5**, the times for completion were found to be 2.0, 1.0 and 0.5 h, respectively, the order of the reactivity decreasing with increase in the bulkiness of R^1. In contrast, the positional isomer of **5** (**8**) showed extremely rapid reaction which was complete in 5 min. The highly reactive behaviour of **8** may be interpreted in terms of the reactive benzylic 3-position and the reduced steric crowding upon rehybridization to a sp^3 bond encountered with the covalent hydroxylation. Since compound **8** was converted into **16** even at room temperature, the ring contraction is not thermally induced. Use of weaker solutions of alkali led to retardation of the reaction, *e.g.* it

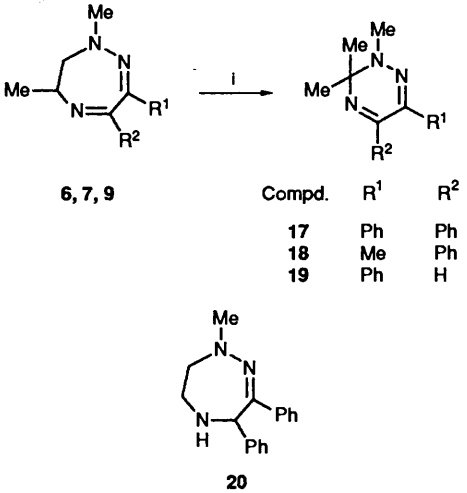
required 4 h in 5% alkali solution and as much as 10 h in a 2% solution at reflux temperature.



Scheme 2 *Reagents:* i, 10% NaOH–EtOH

Prolonged heating caused a decrease in the yield of **10** while that of **13** increased. This strongly suggests that the hydroxylated triazine **10** may convert into the deoxy compound **13**. In fact, exposure of a sample of **10** to the ring-contraction conditions used for the starting triazepine **3**, gave a mixture of **10** and **13**.

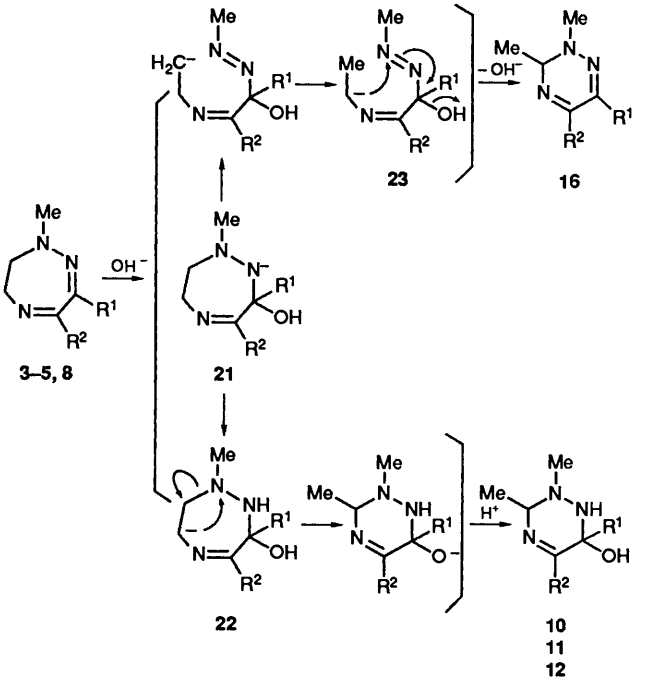
The 6-methyl derivatives **6**, **7** and **9** of **3**, **4** and **8** were exclusively converted into the corresponding gem-dimethyl structures, the results indicating that during ring contraction bond cleavage occurred between the 1 and 7 positions. (Scheme 3).



Scheme 3 *Reagents:* i, 10% NaOH–EtOH

In contrast to the behaviour of the parent compound **3**, the partially reduced product **20**[6] resisted the ring contraction even under the forcing conditions. Thus, the structural requirements for the contraction might be incorporation of a conjugated diazabutadiene system into the seven-membered ring rather than the substitution pattern on the ring.

The reaction may be initiated by attack of a hydroxide on the 3-position of 6,7-dihydro-1-methyl-1*H*-1,2,5-triazepines to form an anion **21** (Scheme 4). With a 4-phenyl substituent present the anion **21** is converted into the ion **22**, the negative charge being delocalized through conjugation with the phenyl group at the 4-position. The ring-contracted products **10–12** might be produced by attack of a negatively charged C-6 on the N-1 with bond cleavage between the 1- and 7-positions. However, when the 4-substituent is other than a phenyl group, the anion **22** cannot be formed. The dihydrotriazine **16** may be produced by the bond cleavage between the positions 1 and 7 possibly induced by migration of the negative charge from the 2-position of the initially formed anion **21**. The primary carbanion rearranges to a secondary anion **23** (by a proton shift) which then attacks the terminal nitrogen with concomitant elimination of the hydroxide. Despite the presence of a 4-phenyl group in the 6-methyl derivatives **6** and **7**, they were converted only into the corresponding 2,3-dihydrotriazines **17** and **18**, no other ring-contracted products being formed. The absence of other dihydro- and tetrahydro-triazines is a likely result of steric constraints on anion **22** formation in which the negative charge at the 6-position would be stabilized.



Scheme 4

The structures of the dihydro- and tetrahydro-triazine products **10–19** were supported by analytical and spectroscopic results. The ^{1}H NMR spectra showed that whilst all the starting dihydrotriazepine substituents **3–9** were incorporated into the corresponding ring-contracted compounds **10–19**, the original ethylene linkage in the ring had disappeared. The tetrahydrotriazines **10–12** each had two exchangeable protons (NH and OH) at δ 7.12–7.90 and the other characteristic signals were at δ 4.19–4.65 (quartet, J 6.0 Hz, 3-H) and 1.43–1.50 (d, J 6.0 Hz, 3-Me). The appearance of a well-resolved quartet (3-H) and a broad singlet at δ 7.39 (6-H) in compound **12** suggests that it has a 1,2,3,6-tetrahydro rather than a 2,3,4,5-tetrahydro

Table 1 Eu-Induced shifts

Compound **5**				
1-Me	7-CH_2	6-CH_2	3-H	4-Ph
3.25 (−0.00)	3.55 (−0.00)	4.14 (−0.00)	6.89 (−0.00)	7.52 (−0.00)
Compound **8**				
1-Me	7-CH_2	6-CH_2	3-Ph	4-H
3.76 (−0.43)	4.58 (−0.98)	6.15 (−2.07)	7.58 (−0.17)	10.24 (−2.08)

Table 2 Experimental data for the preparation of 6,7-dihydro-1*H*-1,2,5-triazepines **4–9**

Compd.	Method	Time (h)	Yield (%)	Column chromatography Eluent* (ratio)
4	A	6	76	a (98:2)
5	B	2	28	a (95:5)
6	A	17	64	b
7	A	17	49	b
8	C	50	59	a (98:2)
9	C	65	50	a (98:2)

*a, $CHCl_3$–MeOH; b, $CHCl_3$.

Table 3 Experimental data for the treatment of 6,7-dihydro-1*H*-1,2,5-triazepines **3–9** with ethanolic sodium hydroxide

Starting compd.	Time (h)	Products (yield %)	Column chromatography Eluent* (ratio)
3	2	**10** (66), **13**-H_2O (15)	a (95:5)
4	2	**11** (27), **14** (60)	a (95:5)
5	1	**12** (29), **15** (29)	a (98:2)
6	17	**17** (86)	b
7	17	**18** (70)	b
8	0.5	**16** (40)	a (98:2)
9	2	**19** (58)	a (98:2)
10	7	**13**-H_2O (27)†	a (95:5)

* a, $CHCl_3$–MeOH; b, $CHCl_3$. † **10** was recovered in 44%.

structure which would be expected to exhibit complex coupling arising from the three adjacent protons. Each of the dihydrotriazines **13–15** had signals in the ranges of δ 4.50–5.65 (exchangeable NH) and 2.07–2.38 (s, 3-Me). The appearance of the methyl protons as a singlet suggests that they should have a 1,2-dihydro structure. An exchangeable proton signal was absent in the spectra of the dihydrotriazines **16–19** which showed for **16** δ 4.57 (quartet, J 6.0 Hz, 3-H) and 1.38 (d, J 6.0 Hz, 3-Me) and for compounds **17–19**, two identical signals in the range δ 1.34–1.37 for the two 3-Me's. This equivalence supports the presence of geminal dimethyls and thus a 2,3-dihydro structure.

Experimental

Microanalyses were performed with a Perkin-Elmer 240D elemental analyser at the Microanalytical Laboratory of Kitasato University. NMR and mass spectra were recorded on Hitachi R-24B and JMS-DX100 instruments, respectively. Column chromatography was performed on silica gel (Wakogel C-200).

Aminoalkylhydrazines.—The aminoalkylhydrazines employed are known compounds and were prepared by a literature method.[7] Compound **1** (88%), a liquid, b.p. 155–161 °C (Found: C, 40.1; H, 12.5; N, 46.9. $C_3H_{11}N_3$ requires C, 40.4; H, 12.4; N, 47.1%); δ_H(60 MHz; $CDCl_3$) 2.28 (4 H, br s, 2 × NH_2), 2.45 (3 H, s, NMe) and 2.45–2.85 (4 H, m, NCH_2CH_2N).

Compound **2** (77%), a liquid, b.p. 97–100 °C/82 mmHg (Found: C, 46.3; H, 12.7; N, 40.2. $C_4H_{13}N_3$ requires C, 46.6; H, 12.7; N, 40.7%); δ_H($CDCl_3$) 1.03 (3 H, d, J 6.0, CH*Me*), 2.26 (2 H, t, J 4.2, NCH_2CHN), 2.28 (4 H, br s, 2 × NH_2), 2.45 (3 H, s, NMe) and 3.00 [1 H, m, NCH_2CH(Me)N].

*6,7-Dihydro-1-methyl-*1H*-1,2,5-triazepines.*—Compound **3** is a known compound and was prepared according to the literature method.[6] Compound **3** (84%), yellow plates, m.p. 115–116 °C (from propan-1-ol) (Found: C, 77.7; H, 6.5; N, 15.8. $C_{17}H_{17}N_3$ requires C, 77.5; H, 6.5; N, 16.0%); δ_H($CDCl_3$) 2.95 (3 H, s, NMe), 3.58 [2 H, m, N(Me)CH_2CH_2N], 3.88 [2 H, m, N(Me)CH_2CH_2N] and 7.23–7.48 (10 H, m, 2 × Ph); *m/z* 263 (M^+, 21%), 235 (100) and 117 (95).

*General Procedure for the Preparation of 6,7-Dihydro-*1H*-1,2,5-triazepines* **4–9**.—(A) A mixture of compound **1** or **2** (3 mmol), benzil or 1-phenylpropane-1,2-dione (3 mmol), toluene-*p*-sulfonic acid monohydrate (0.06 g) and benzene (70 cm^3) was heated under reflux for 6–17 h with azeotropic removal of water and then evaporated. The residual oil was subjected to column chromatography.

(B) Phenylglyoxal monohydrate (5 mmol) was dissolved in chloroform (50 cm^3) and to the solution was added compound **1** (5 mmol). The mixture was dried (Na_2SO_4) after 0.5 h at 10 °C and toluene-*p*-sulfonic acid monohydrate (0.1 g) was added to it. The mixture was then heated under reflux for 2 h after which it was evaporated under reduced pressure and the residual oil was subjected to column chromatography.

(C) A mixture of compound **1** or **2** (2 mmol), phenylglyoxal diethyl acetal (2 mmol), toluene-*p*-sulfonic acid monohydrate (0.5 mmol) and chloroform (50 cm^3) was heated under reflux for 50–65 h and then evaporated. The residual oil was subjected to column chromatography.

*6,7-Dihydro-1,3-dimethyl-4-phenyl-*1H*-1,2,5-triazepine* **4**. Yellow oil (Found: C, 71.5; H, 7.5; N, 20.5. $C_{12}H_{15}N_3$ requires C, 71.6; H, 7.5; N, 20.9%); δ_H($CDCl_3$) 2.04 (3 H, s, Me), 2.82 (3 H, s, NMe), 3.38 [2 H, m, N(Me)CH_2CH_2N], 3.69 [2 H, m, N(Me)CH_2CH_2N] and 7.40 (5 H, m, Ph); *m/z* 201 (M^+, 38%), 173 (100) and 117 (100).

*6,7-Dihydro-1-methyl-4-phenyl-*1H*-1,2,5-triazepine* **5**. Yellow oil (Found: C, 70.6; H, 7.0; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.4%); δ_H($CDCl_3$) 3.25 (3 H, s, NMe), 3.55 [2 H, m, N(Me)CH_2CH_2N], 4.14 [2 H, m, N(Me)CH_2CH_2N], 6.89 (1 H, s, 3-H), 7.38 (3 H, m, Ph) and 7.65 (2 H, m, Ph); *m/z* 187 (M^+, 100%), 159 (67), 145 (56) and 117 (74).

*6,7-Dihydro-1-methyl-3-phenyl-*1H*-1,2,5-triazepine* **8**. Yellow oil (Found: C, 70.5; H, 7.0; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.4%); δ_H($CDCl_3$) 3.33 (3 H, s, NMe), 3.60 [2 H, m, N(Me)CH_2CH_2N], 4.08 [2 H, m, N(Me)CH_2CH_2N], 7.41 (5 H, m, Ph) and 8.16 (1 H, s, 4-H); *m/z* 187 (M^+, 86%), 159 (100) and 145 (60).

*6,7-Dihydro-1,6-dimethyl-3,4-diphenyl-*1H*-1,2,5-triazepine* **6**. Pale yellow prisms, m.p. 87–89 °C (Found: C, 77.9; H, 6.9; N, 15.1. $C_{18}H_{19}N_3$ requires C, 77.9; H, 6.9; N, 15.15%); δ_H ($CDCl_3$) 1.44 (3 H, d, J 5.4, CH*Me*), 2.88 (3 H, s, NMe), 3.15–3.70 [3 H, m, NCH_2CH(Me)N], 7.15 (6 H, m, 2 × Ph) and 7.47 (4 H, m, 2 × Ph); *m/z* 277 (M^+, 7%), 235 (100) and 131 (21).

6,7-*Dihydro*-1,3,6-*trimethyl*-4-*phenyl*-1H-1,2,5-*triazepine* **7**. Yellowish brown oil (Found: C, 72.45; H, 7.9; N, 19.4. $C_{13}H_{17}N_3$ requires C, 72.5; H, 8.0; N, 19.5%); $\delta_H(CDCl_3)$ 1.39 (3 H, d, *J* 5.4, CH*Me*), 1.97 (3 H, s, Me), 2.73 (3 H, s, NMe), 2.98–3.45 [3 H, m, NC*H*$_2$C*H*(Me)N] and 7.37 (5 H, m, Ph); *m*/*z* 215 (M^+, 47%), 173 (100) and 131 (100).

6,7-*Dihydro*-1,6-*dimethyl*-3-*phenyl*-1H-1,2,5-*triazepine* **9**. Yellowish brown oil (Found: C, 71.5; H, 7.5; N, 20.9. $C_{12}H_{15}N_3$ requires C, 71.6; H, 7.5; N, 20.9%); $\delta_H(CDCl_3)$ 1.32 (3 H, d, *J* 6.6, CH*Me*), 3.33 (3 H, s, NMe), 3.32 [2 H, m, NC*H*$_2$CH(Me)N], 4.07 [1 H, m, NCH$_2$C*H*(Me)N], 7.40 (5 H, m, Ph) and 8.10 (1 H, s, CH); *m*/*z* 201 (M^+, 23%) and 159 (100).

4,5,6,7-*Tetrahydro*-1-*methyl*-1H-1,2,5-*triazepines*.—Compound **20** is known compound and was prepared according to the literature method.[6] Compound **20** (19%), pale yellow plates, m.p. 112–114 °C (Found: C, 77.0; H, 7.25; N, 15.8. $C_{17}H_{19}N_3$ requires C, 76.95; H, 7.2; N, 15.8%); $\delta_H(CDCl_3)$ 2.10 (1 H, s, NH), 2.81 (4 H, m, NCH$_2$CH$_2$N), 3.03 (3 H, s, NMe), 5.44 (1 H, s, NCH) and 7.34 (10 H, m, 2 × Ph); *m*/*z* 265 (M^+, 5%), 234 (39) and 119 (61).

General Procedure for the Treatment of 6,7-*Dihydro*-1H-1,2,5-*triazepines* **3–9** *with Ethanolic Sodium Hydroxide*.—Sodium hydroxide (2 g) was dissolved in ethanol (22 cm^3) and the triazepine (1 mmol) was added to the solution. The solution was heated under reflux for 0.5–17 h after which it was neutralized with 20% hydrochloric acid. The precipitated sodium chloride was filtered off and the filtrate was evaporated under reduced pressure. The residual oil was then subjected to column chromatography.

1,2,3,6-*Tetrahydro*-6-*hydroxy*-2,3-*dimethyl*-5,6-*diphenyl*-1,2,4-*triazine* **10**. Yellow oil (Found: C, 72.5; H, 6.8; N, 14.8. $C_{18}H_{19}N_3O$ requires C, 72.6; H, 6.8; N, 14.9%); $\delta_H(CDCl_3)$ 1.50 (3 H, d, *J* 6.0, CH*Me*), 3.17 (3 H, s, NMe), 4.46 (1 H, q, *J* 6.0, C*H*Me), 7.19 (5 H, s, Ph), 7.20 (5 H, s, Ph) and 7.12–7.40 (2 H, br, NH and OH); *m*/*z* 263 ($M^+ - H_2O$, 8%), 248 (55) and 105 (100).

1,2-*Dihydro*-2,3-*dimethyl*-5,6-*diphenyl*-1,2,4-*triazine* **13** *monohydrate*. Needles, m.p. 118–119 °C (Found: C, 72.5; H, 6.9; N, 14.8. $C_{17}H_{17}N_3 \cdot H_2O$ requires C, 72.6; H, 6.8; N, 14.9%); $\delta_H(CDCl_3)$ 2.07 (3 H, s, Me), 2.64 (2 H, br s, H_2O), 3.39 (3 H, s, NMe), 5.65 (1 H, br s, NH), 7.24 (6 H, m, 2 × Ph) and 7.66 (4 H, m, 2 × Ph); *m*/*z* 263 (M^+, 100%), 186 (100), 178 (99) and 56 (100).

1,2,3,6-*Tetrahydro*-6-*hydroxy*-2,3,6-*trimethyl*-5-*phenyl*-1,2,4-*triazine* **11**. Yellow oil (Found: C, 65.8; H, 7.8; N, 19.1. $C_{12}H_{17}N_3O$ requires C, 65.7; H, 7.8; N, 19.2%); $\delta_H(CDCl_3)$ 1.44 (3 H, d, *J* 6.0, CH*Me*), 1.99 (3 H, s, Me), 2.98 (3 H, s, NMe), 4.19 (1 H, q, *J* 6.0, C*H*Me), 7.35 (5 H, s, Ph), 7.35 and 7.90 (2 H, br, NH and OH); *m*/*z* 201 ($M^+ - H_2O$, 9%) and 186 (100).

1,2-*Dihydro*-2,3,6-*trimethyl*-5-*phenyl*-1,2,4-*triazine* **14**. Pale yellow powder, m.p. 134–136 °C (Found: C, 71.4; H, 7.5; N, 20.8. $C_{12}H_{15}N_3$ requires C, 71.6; H, 7.5; N, 20.9%); $\delta_H(CDCl_3)$ 2.30 (3 H, s, Me), 2.33 (3 H, s, Me), 2.70 (3 H, s, NMe), 4.50 (1 H, br s, NH), 7.28 (3 H, m, Ph) and 7.58 (2 H, m, Ph); *m*/*z* 201 (M^+, 100%), 130 (18), 115 (40), 104 (38) and 57 (73).

1,2,3,6-*Tetrahydro*-6-*hydroxy*-2,3-*dimethyl*-5-*phenyl*-1,2,4-*triazine* **12**. Yellow oil (Found: C, 64.4; H, 7.35; N, 20.4. $C_{11}H_{15}N_3O$ requires C, 64.4; H, 7.4; N, 20.5%); $\delta_H(CDCl_3)$ 1.43 (3 H, d, *J* 6.0, CH*Me*), 3.14 (3 H, s, NMe), 4.65 (1 H, q, *J* 6.0, C*H*Me), 7.43 (3 H, m, Ph), 7.80 (2 H, m, Ph) and 7.30–7.50 (3 H, m, 6-H, NH and OH); *m*/*z* 188 ($M^+ - OH$, 4%) and 172 (100).

1,2-*Dihydro*-2,3-*dimethyl*-5-*phenyl*-1,2,4-*triazine* **15**. Oil (Found: C, 70.6; H, 7.0; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.4%); $\delta_H(CDCl_3)$ 2.38 (3 H, s, Me), 2.84 (3 H, s, NMe), 4.50 (1 H, br s, NH), 7.33 (4 H, m, 6-H and Ph) and 7.69 (2 H, m, Ph); *m*/*z* 187 (M^+, 100%), 103 (29) and 57 (82).

2,3-*Dihydro*-2,3-*dimethyl*-6-*phenyl*-1,2,4-*triazine* **16**. Yellow oil (Found: C, 70.5; H, 7.0; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.4%); $\delta_H(CDCl_3)$ 1.38 (3 H, d, *J* 6.0, CH*Me*), 3.21 (3 H, s, NMe), 4.57 (1 H, q, *J* 6.0, C*H*Me), 7.33 (3 H, m, Ph), 7.69 (2 H, m, Ph) and 7.86 (1 H, s, 5-H); *m*/*z* 187 (M^+, 46%) and 172 (100).

2,3-*Dihydro*-2,3,3-*trimethyl*-5,6-*diphenyl*-1,2,4-*triazine* **17**. Pale yellow plates, m.p. 120–122 °C (Found: C, 77.9; H, 6.9; N, 15.1. $C_{18}H_{19}N_3$ requires C, 77.9; H, 6.9; N, 15.1%); $\delta_H(CDCl_3)$ 1.47 (6 H, s, 2 × Me), 3.28 (3 H, s, NMe), 7.18 (5 H, s, Ph) and 7.21 (5 H, s, Ph); *m*/*z* 277 (M^+, 9%), 262 (100), 246 (75) and 234 (48).

2,3-*Dihydro*-2,3,3,6-*tetramethyl*-5-*phenyl*-1,2,4-*triazine* **18**. Pale yellow plates, m.p. 49–51 °C (Found: C, 72.5; H, 8.0; N, 19.5. $C_{13}H_{17}N_3$ requires C, 72.5; H, 8.0; N, 19.5%); $\delta_H(CDCl_3)$ 1.34 (6 H, s, 2 × Me), 1.95 (3 H, s, Me), 3.03 (3 H, s, NMe) and 7.32 (5 H, s, Ph); *m*/*z* 215 (M^+, 37%), 200 (100), 172 (23), 115 (96) and 56 (100).

2,3-*Dihydro*-2,3,6-*trimethyl*-6-*phenyl*-1,2,4-*triazine* **19**. Light brown oil (Found: C, 71.7; H, 7.5; N, 20.8. $C_{12}H_{15}N_3$ requires C, 71.6; H, 7.5; N, 20.9%); $\delta_H(CDCl_3)$ 1.37 (6 H, s, 2 × Me), 3.18 (3 H, s, NMe), 7.26 (3 H, m, Ph), 7.56 (2 H, m, Ph) and 7.78 (1 H, s, 5-H); *m*/*z* 201 (M^+, 100%), 186 (100), 172 (27), 158 (42) and 56 (41).

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