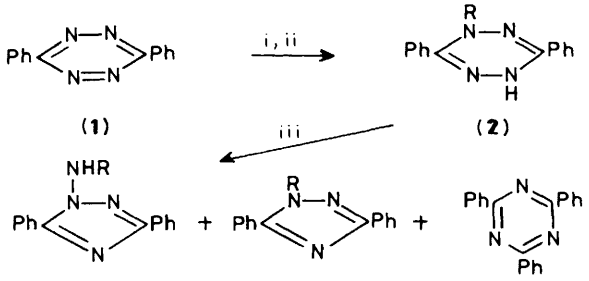
Rearrangement Reactions of 1,3,6-Triaryl-1,4-dihydro-*s*-tetrazines leading to 2,4-Diarylquinazolines, 1-Anilino-3,5-diaryl-1*H*-1,2,4-triazoles, 1,3,5-Triaryl-1*H*-1,2,4-triazoles, and 2,5-Diaryl-1*H*-1,3,4-oxadiazoles. *X*-Ray Structure Determination of 6-Isopropyl-2,4-diphenylquinazoline

Daniel Hunter, Douglas G. Neilson,* and Timothy J. R. Weakley
Department of Chemistry, The University, Dundee DD1 4HN

1,3,6-Triaryl-1,4-dihydro-*s*-tetrazines (**2c—g**) rearrange on heating at *ca.* 200 °C to 2,4-diarylquinazolines (for which an *X*-ray determination was carried out on the 6-isopropyl compound) and 1-anilino-3,5-diaryl-1*H*-1,2,4-triazoles as major products. Hydrolysis in chloroform solution of the title compounds (**2**) and their 1-alkyl analogues gives rise to 1-aryl (or alkyl)-3,5-diaryl-1*H*-1,2,4-triazoles and 2,5-diaryl-1,3,4-oxadiazoles.

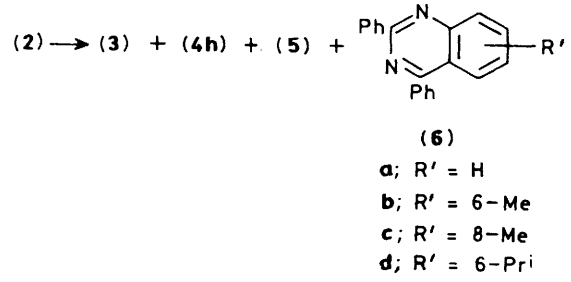
Recent work[1,2] has shown unambiguously that both alkyl and aryl Grignard reagents react with 3,6-diaryl-*s*-tetrazines, *e.g.* (**1**), by attacking at ring nitrogen to give 1-alkyl (or aryl)-3,6-diaryl-1,4-dihydro-*s*-tetrazines (**2**). In our initial studies[1] on the thermal rearrangement of such compounds (**2**) we reported that the 1-alkyl-1,4-dihydro-*s*-tetrazines (**2a**) and (**2b**) gave as principal products the 1-alkylamino-1*H*-1,2,4-triazoles (**3a**) and (**3b**) and the 1-alkyl-1*H*-1,2,4-triazoles (**4a**) and (**4b**) along with smaller amounts of 3,5-diphenyl-1*H*-1,2,4-triazole (**4h**) and 2,4,6-triphenyl-*s*-triazine (**5**), (Scheme 1). Mechanistic pathways



Scheme 1. *Reagents:* i, RMgBr; ii, H_3O^+; iii, heat

involving betaines and 1,3-dipolar species were proposed for the formation of all of these compounds.[1] However, in that paper,[1] we also reported that the thermal decomposition of 1,3,6-triaryl-1,4-dihydro-*s*-tetrazines (**2c—g**) followed a somewhat different reaction pathway and it is the chemistry of these thermal decomposition reactions, among others, which we now describe.

Thermolysis Reactions of 1,3,6-*Triaryl*-1,4-*dihydro*-s-*tetrazines*.—Thermolysis of the 1,3,6-triaryl-1,4-dihydro-*s*-tetrazines (**2c—f**) at *ca.* 195 °C for 15 min yielded the 1-anilino-3,5-diaryl-1*H*-1,2,4-triazoles (**3c—f**) and the 2,4-diarylquinazolines (**6a—d**) as the major products along with, in some instances, trace amounts of 3,5-diphenyl-1*H*-1,2,4-triazole (**4h**) and the *s*-

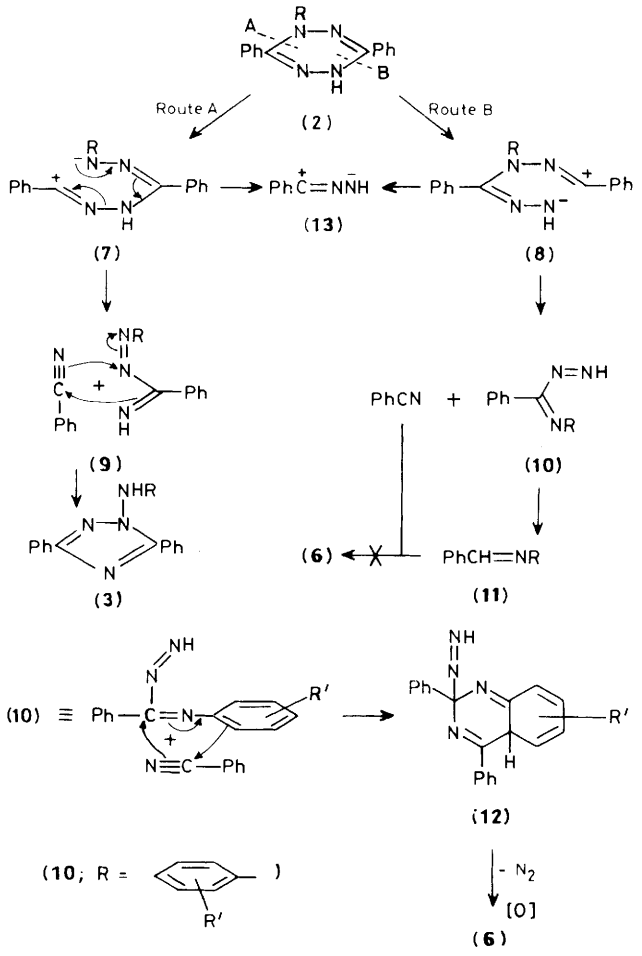


Scheme 2.

triazine (**5**) (Scheme 2). Of these products, the quinazolines, which were identified initially by *X*-ray analysis of compound (**6d**) and later by synthesis of compound (**6a**) (see later), do not occur in the rearrangement reactions of the corresponding 1-alkyl-3,6-diaryl-1,4-dihydro-*s*-tetrazines[1] (**2a,b**) where the 1-alkyl-3,5-diphenyl-1*H*-1,2,4-triazoles (**4a,b**) are found instead and hence a new reaction pathway operates in the case of the 1-aryl series (**2c—g**).

The formation of 2,4,6-triphenyl-*s*-triazine (**5**) along with the nature of some of the other products suggests the formation of phenyl cyanide (although it itself was not identified) from the thermal decomposition of the dihydrotetrazines (**2**). Scheme 3 illustrates two possible fission modes for species (**2**), (a) cleavage of a C–NR bond (route A) or (b) cleavage of a C–NH bond (route B). Routes A and B give rise, respectively, to the betaines (**7**) and (**8**) which in turn yield phenyl cyanide and the isomeric dehydroamidrazones (**9**) and (**10**). Betaines of the type (**7**) and (**8**) have been postulated by Birkofer[3] and Huisgen[4] in closely related work and have been suggested earlier by us[1] to explain the formation of 1-alkylamino-1*H*-1,2,4-triazoles (as illustrated in Scheme 3, route A). Hence it is envisaged that the 1-arylamino analogues (**3**; R = aryl) are also formed in this manner analogously to their 1-alkyl counterparts.

One possible route to the quinazolines (**6**) would involve the dehydroamidrazone (**10**) losing nitrogen and yielding the imine (**11**)—a route proposed by Huisgen[4] to explain his products of thermolysis of 1,4-dihydro-3,6-diphenyl-*s*-tetrazine (**2h**). However, in a separate experiment we found that the imine (**11**) and phenyl cyanide failed to condense under conditions analogous to those used in the thermolyses. Alternatively, it is possible for the dehydroamidrazone (**10**) to be attacked by nitrile, before loss of nitrogen, and to give the intermediate (**12**) which, by oxidative loss of nitrogen, forms the quinazoline (**6**) (Scheme 3). The trace quantities of 3,5-diphenyl-1*H*-1,2,4-triazole (**4h**) can

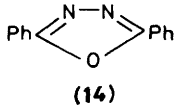


Scheme 3.

arise from phenyl cyanide[1,5,6] reacting with the dipolar intermediate (**13**) formed by breakdown of the betaine (**8**) (Scheme 3). This cleavage route appears important for the betaine (**8**; R = alkyl) but in view of the trace amounts of the triazole (**4h**) and the absence of 1-aryl-3,5-diphenyl-1*H*-1,2,4-triazoles (**4**; R = aryl) is not important for (**8**; R = aryl).

Rearrangement Reactions of 1,4-*Dihydro*-3,6-*diphenyl*-s-*tetrazines in Chloroform or Dichloromethane Solutions.*—During the course of these and our earlier studies[1] it was noticed that chloroform solutions of compounds of type (**2**; R = H, alkyl, or aryl) changed in colour from yellow to red on being kept. At first it was considered that this was a light-induced reaction but later it was discovered that the reaction also proceeded in the dark and was unaffected by the presence of tri-(t-butyl)phenol. The transformation did not take place in ethanol or tetrahydrofuran but could be carried out in dichloromethane.

The red product in each case, irrespective of starting material, was identified as 3,6-diphenyl-*s*-tetrazine (**1**) and it was found to be accompanied by 2,5-diphenyl-1,3,4-oxadiazole (**14**) and, except in the case of starting material (**2h**), the corresponding 1-alkyl or -aryl-3,5-diphenyl-1*H*-1,2,4-triazole (**4b** or **d**).



(**14**)

It is envisaged that the dihydrotetrazines (**2**; R = alkyl or aryl) cleave to give two 1,3-dipolar species $PhC^{+}=N\bar{N}H$ (**13**) (Scheme 3) and $PhC^{+}=N\bar{N}R$ (**15**). Dimerisation of species (**13**) gives the dihydrotetrazine (**2h**) which is readily oxidised to 3,6-diphenyl-*s*-tetrazine (**1**). The other 1,3-dipolar intermediates (**15**) act as precursors of the 1-substituted 1,2,4-triazoles (**4**) through interaction with phenyl cyanide.[5,6]

As the rearrangement reaction does not take place in *anhydrous* chloroform, the formation of 2,5-diphenyl-1,3,4-oxadiazole (**14**) could take place by direct hydrolysis of the dihydrotetrazines (**2**) (favoured in acid conditions[1]), but might also arise by hydrolysis in dilute solution of 3,6-diphenyl-*s*-tetrazine (**1**) (one of the reaction products). This latter process is more favoured under basic conditions.[7–9]

X-Ray Structure of 6-*Isopropyl*-2,4-*diphenylquinazoline* (**6d**).—As more than one feasible, fused aromatic structure could be written for the compound $C_{23}H_{20}N_2$ obtained by thermal rearrangement of the dihydrotetrazine (**2f**) an *X*-ray crystallographic study was carried out on this product which was shown to have the quinazoline structure (**6d**). Only one other *X*-ray determination, namely that by Huiszoon,[10] has been made of simple quinazoline structures and this relates to the parent compound, quinazoline, itself. Bond angles and bond lengths determined in this work bear good agreement with those reported by Huiszoon.[10] In addition, the 2-phenyl substituent is twisted 3.8° out of the plane of the pyrimidine ring but the more crowded 4-phenyl substituent lies at an angle of 63.9° to the pyrimidine ring but there are no close interactions (Figure). The two aromatic rings of quinazoline are folded by 4.5°.

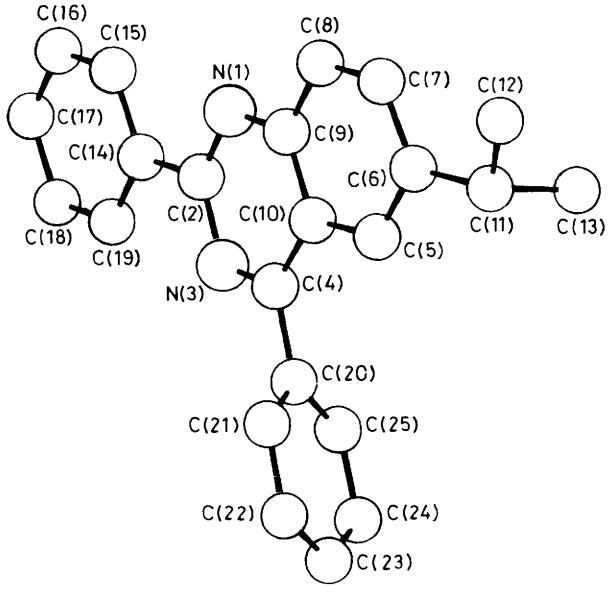


Figure. *X*-Ray molecular structure of 6-isopropyl-2,4-diphenylquinazoline (**6d**)

Experimental

M.p.s are uncorrected. ^{1}H N.m.r. spectra were run on a Varian EM 360 (60 MHz) instrument.

Preparation of 3,6-*Diphenyl*-s-*tetrazine* (**1**).—The tetrazine (**1**) was prepared by a literature method,[11] and had m.p. 196—198 °C (lit.,[12] 198 °C).

Preparation of 1-*Substituted* 1,4-*Dihydro*-3,6-*diphenyl*-s-*tetrazines* (**2**).—The action of Grignard reagents on the tetrazine (**1**) (0.46 g) by the method previously reported[1] yielded the compounds (**2**) as below.

1,4-*Dihydro*-1-*isopropyl*-3,6-*diphenyl*-s-*tetrazine* (**2b**). The Grignard reagent was prepared from 2-bromopropane. Compound (**2b**) (0.27 g) had m.p. 172—173 °C (lit.,[1] 172—173 °C).

1,4-*Dihydro*-1,3,6-*triphenyl*-s-*tetrazine* (**2c**). The Grignard reagent was prepared from bromobenzene. Compound (**2c**) (0.57 g) had m.p. 124—125 °C (lit.,[13] 125—126 °C).

1,4-*Dihydro*-3,6-*diphenyl*-1-(p-*tolyl*)-s-*tetrazine* (**2d**). The Grignard reagent was prepared from 4-bromotoluene. Compound (**2d**) (0.46 g) had m.p. 188 °C (lit.,[1] 188 °C).

1,4-*Dihydro*-3,6-*diphenyl*-1-(o-*tolyl*)-s-*tetrazine* (**2e**). The Grignard reagent was prepared from 2-bromotoluene. *Compound* (**2e**) (0.23 g) had m.p. 141—142 °C [from light petroleum (b.p. 80—100 °C)]; $\delta_H(CDCl_3)$ 2.0 (3 H, s, Me) and 6.9—7.8 (15 H, m, ArH and NH); $\nu_{max.}$(Nujol) 3 270 cm^{-1} (NH) (Found: C, 77.9; H, 6.1; N, 16.7. $C_{21}H_{18}N_4$ requires C, 77.3; H, 5.6; N, 17.2%).

1-(p-*Cumenyl*)-1,4-*dihydro*-3,6-*diphenyl*-s-*tetrazine* (**2f**). The Grignard reagent was prepared from *p*-bromocumene.[14] *Compound* (**2f**) (0.44 g) had m.p. 135—136 °C [from light petroleum (b.p. 80—100 °C)]; $\delta_H(CDCl_3)$ 1.2 (6 H, d, 2 × Me), 2.8 (1 H, septet, C*H*Me_2), 7.0—7.8 (14 H, m, ArH), and 7.6 (1 H, s, NH); $\nu_{max.}$(Nujol) 3 300 cm^{-1} (NH) (Found: C, 78.1; H, 6.3; N, 15.8. $C_{23}H_{22}N_4$ requires C, 78.0; H, 6.2; N, 15.8%).

1,4-*Dihydro*-3,6-*diphenyl*-1-(p-*t-butylphenyl*)-s-*tetrazine* (**2g**). The Grignard reagent was prepared from 4-bromo-t-butylbenzene.[15] *Compound* (**2g**) (0.48 g) had m.p. 156 °C (from acetone); $\delta_H(CDCl_3)$ 1.3 (9 H, s, 3 × Me), 7.1—7.7 (14 H, m, ArH), and 7.6 (1 H, s, NH); $\nu_{max.}$(Nujol) 3 290 cm^{-1} (NH); despite several attempts, good analysis figures could not be obtained (Found: C, 78.7; H, 7.1; N, 14.4. $C_{24}H_{24}N_4$ requires C, 78.3; H, 6.5; N, 15.2%).

Thermolysis of the Dihydrotetrazines (**2**).—The dihydrotetrazine (**2**) (0.5 g) was heated in an oil-bath at 190—200 °C (bath temperature) for 15 min. On cooling, a glassy product formed which was dissolved in acetone and separated chromatographically [silica; eluted with diethyl ether–light petroleum (b.p. 40—60 °C) (1:3)]. The products obtained were as below.

From 1,4-*dihydro*-1,3,6-*triphenyl*-s-*tetrazine* (**2c**). (i) 2,4-Diphenylquinazoline (**6a**) (87 mg) had m.p. 116—117 °C (lit.,[16] 119 °C) and was identical with compound (**6a**) prepared by an independent route;[16] $\nu_{max.}$(Nujol) 1 530 cm^{-1}.

(ii) 1-*Anilino*-3,5-*diphenyl*-1*H*-1,2,4-*triazole* (**3c**) (152 mg) had m.p. 151—153 °C [from light petroleum (b.p. 80—100 °C)]; $\delta_H(CDCl_3)$ 6.4—8.1 (15 H, m, 3 × Ph) and 7.5 (1 H, s, NH); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH) (Found: C, 76.9; H, 5.2; N, 18.0. $C_{20}H_{16}N_4$ requires C, 76.9; H, 5.1; N, 17.9%).

(iii) 3,5-Diphenyl-1*H*-1,2,4-triazole (**4h**) which was identified by t.l.c. [diethyl ether–light petroleum (b.p. 40—60 °C) (1:1)].

From 1,4-*dihydro*-3,6-*diphenyl*-1-(p-*tolyl*)-s-*tetrazine* (**2d**). (i) 6-Methyl-2,4-diphenylquinazoline (**6b**) (120 mg) had m.p. 180—181 °C (lit.,[16] 177 °C); $\delta_H(CDCl_3)$ 2.5 (3 H, s, Me) and 7.4—8.7 (13 H, m, ArH); $\nu_{max.}$(Nujol) 1 530 cm^{-1} (Found: C, 84.6; H, 5.4; N, 9.4. Calc. for $C_{21}H_{16}N_2$: C, 85.1; H, 5.4, N, 9.5%).

(ii) 3,5-*Diphenyl*-1-(p-*toluidino*)-1H-1,2,4-*triazole* (**3d**) (57 mg) had m.p. 128—130 °C [from light petroleum (b.p. 80—100 °C)]; $\delta_H(CDCl_3)$ 2.2 (3 H, s, Me), 6.3—8.1 (14 H, m, ArH), and 7.7 (1 H, s, NH); $\nu_{max.}$(Nujol) 3 200 and 3 210 cm^{-1} (NH) (Found: M^+, 326.152 346. $C_{21}H_{18}N_4$ requires *M*, 326.153 13).

(iii) 3,5-Diphenyl-1*H*-1,2,4-triazole (**4h**) which was identified by t.l.c. [diethyl ether–light petroleum (b.p. 40—60 °C) (1:3)].

(iv) 2,4,6-Triphenyl-*s*-triazine (**5**) which was identified by t.l.c. [diethyl ether–light petroleum (b.p. 40—60 °C) (1:3); or carbon tetrachloride].

From 1,4-*dihydro*-3,6-*diphenyl*-1-(o-*tolyl*)-s-*tetrazine* (**2e**). (i) 8-*Methyl*-2,4-*diphenylquinazoline* (**6c**) (98 mg) had m.p. 123 °C (from methanol); $\delta_H(CDCl_3)$ 2.9 (3 H, s, Me) and 7.4—8.7 (13 H, m, ArH); $\nu_{max.}$(Nujol) 1 530 cm^{-1} (Found: C, 84.9; H, 5.5; N, 9.6. $C_{21}H_{16}N_2$ requires C, 85.1; H, 5.4; N, 9.5%).

(ii) 3,5-*Diphenyl*-1-(o-*toluidino*)-1H-1,2,4-*triazole* (**3e**) (126 mg) had m.p. 130—131 °C [from light petroleum (b.p. 80—100 °C)]; $\delta_H(CDCl_3)$ 2.3 (3 H, s, Me) and 7.0—8.2 (15 H, m, ArH and NH); $\nu_{max.}$(Nujol) 3 310 cm^{-1} (NH) (Found: C, 76.8; H, 5.7; N, 17.0. $C_{21}H_{18}N_4$ requires C, 77.3; H, 5.5; N, 17.2%).

(iii) 3,5-Diphenyl-1*H*-1,2,4-triazole (**4h**) which was identified by t.l.c. [diethyl ether–light petroleum (b.p. 40—60 °C) (1:3)].

From 1-(p-*cumenyl*)-1,4-*dihydro*-3,6-*diphenyl*-s-*tetrazine* (**2f**). (i) 6-*Isopropyl*-2,4-*diphenylquinazoline* (**6d**) (220 mg) had m.p. 78 °C (from methanol); $\delta_H(CDCl_3)$ 1.3 (6 H, d, 2 × Me), 3.0 (1 H, septet, C*H*Me_2), and 7.4—8.7 (13 H, m, ArH); $\nu_{max.}$(Nujol) 1 530 cm^{-1} (Found: C, 84.7; H, 6.2; N, 8.5. $C_{23}H_{20}N_2$ requires C, 85.2; H, 6.2; N, 8.6%).

Decompositon of 1,4-*Dihydro*-3,6-*diphenyl*-s-*tetrazines* (**2**) *in Chloroform Solution*.—The dihydrotetrazine (**2**) (0.5 g) was dissolved in chloroform (100 ml) and the solution was left in the dark for 6 weeks. The products were separated by chromatography [silica; elution with diethyl ether–light petroleum (b.p. 40—60 °C) (1:3)] as below.

From 1,4-*dihydro*-1-*isopropyl*-3,6-*diphenyl*-s-*tetrazine* (**2b**). (i) 3,6-Diphenyl-*s*-tetrazine (**1**) (70 mg) was identical with compound (**1**) prepared by an independent route.[11]

(ii) A mixture of 2,5-diphenyl-1,3,4-oxadiazole (**14**) (16 mg) and 1-isopropyl-3,5-diphenyl-1*H*-1,2,4-triazole (**4b**) (40 mg), identified by t.l.c. and by comparison of i.r. and n.m.r. spectra with those of compounds (**14**) and (**4b**) prepared by independent routes.[1] The mixture could not be separated by chromatography and the yields quoted are on the basis of integrals of the n.m.r. spectrum of the mixture.

From 1,4-*dihydro*-3,6-*diphenyl*-1-(p-*tolyl*)-s-*tetrazine* (**2d**). (i) 3,6-Diphenyl-*s*-tetrazine (**1**) (51 mg) was identical with compound (**1**) prepared by an independent route.[1]

(ii) 3,5-Diphenyl-1-(*p*-tolyl)-1*H*-1,2,4-triazole (**4d**) (64 mg) had m.p. 109 °C (from ethanol) (lit.,[17] 109 °C); $\delta_H(CDCl_3)$ 2.4 (3 H, s, Me) and 7.2—8.3 (14 H, m, ArH) (Found: C, 81.0; H, 5.5; N, 13.5. Calc for $C_{21}H_{17}N_3$: C, 81.0; H, 5.5; N, 13.5%).

(iii) 2,5-Diphenyl-1,3,4-oxadiazole (**14**) (134 mg) was identical with compound (**14**) prepared by an independent route.[1]

From 1,4-*dihydro*-3,6-*diphenyl*-s-*tetrazine* (**2h**). (i) 3,6-Diphenyl-*s*-tetrazine (**1**) (47 mg) was identical with compound (**1**) prepared by an independent route.[1]

(ii) 2,5-Diphenyl-1,3,4-oxadiazole (**14**) (27 mg) was identical with compound (**14**) prepared by an independent route.[1]

(iii) Unchanged 1,4-dihydro-3,6-diphenyl-*s*-tetrazine (**2h**) (315 mg).

From 1-(p-*cumenyl*)-1,4-*dihydro*-3,6-*diphenyl*-s-*tetrazine* (**2f**). (i) 1-(*p*-Cumenyl)-3,5-diphenyl-1*H*-1,2,4-triazole (**4f**) (7 mg); $\delta_H(CDCl_3)$ 1.3 (6 H, d, 2 × Me), 2.9 (1 H, septet, C*H*Me_2), and 7.2—8.2 (14 H, m, ArH).

(ii) 2,5-Diphenyl-1,3,4-oxadiazole (**14**) (120 mg) was identical with compound (**14**) prepared by an independent route.[1]

When this experiment was repeated (a) in the presence of 2,4,6-tri-(t-butyl)phenol, (b) using dichloromethane in place of chloroform, and (c) in the presence of added water, the results were substantially the same as indicated above. When the experiment was repeated using chloroform dried over phosphorus pentaoxide, however, no reaction took place and the starting material (**2f**) was recovered.

Preparation of N-*Benzylideneaniline*.—Benzaldehyde (1.06 g) and anhydrous calcium chloride (2 g) were stirred together at room temperature, and aniline (0.93 g) was then added all at

Table 1. Atomic co-ordinates $\times 10^4$ for non-hydrogen atoms

	x	*y*	*z*
N(1)	2 561(14)	3 311(5)	3 399(3)
C(2)	1 873(16)	3 609(6)	3 879(4)
N(3)	3 011(14)	3 401(5)	4 526(3)
C(4)	4 946(16)	2 827(7)	4 680(3)
C(5)	7 714(17)	1 835(7)	4 324(4)
C(6)	8 362(17)	1 465(6)	3 829(4)
C(7)	7 176(19)	1 774(8)	3 194(4)
C(8)	5 316(19)	2 389(7)	3 056(4)
C(9)	4 540(17)	2 741(7)	3 555(4)
C(10)	5 823(16)	2 486(6)	4 199(4)
C(11)	10 241(20)	692(8)	3 978(5)
C(12)	11 466(24)	579(10)	3 489(7)
C(13)	8 932(26)	−194(10)	3 996(7)
C(14)	−272(15)	4 214(6)	3 730(4)
C(15)	−1 432(16)	4 490(7)	3 096(4)
C(16)	−3 467(19)	5 045(7)	2 955(5)
C(17)	−4 399(19)	5 333(8)	3 427(5)
C(18)	−3 209(17)	5 079(7)	4 056(5)
C(19)	−1 181(15)	4 515(6)	4 200(4)
C(20)	6 153(14)	2 686(6)	5 382(3)
C(21)	8 539(16)	2 962(7)	5 689(4)
C(22)	9 683(18)	2 807(7)	6 357(4)
C(23)	8 420(15)	2 353(6)	6 692(4)
C(24)	6 078(18)	2 057(7)	6 392(5)
C(25)	4 911(17)	2 244(7)	5 730(4)

once. The mixture was then stirred at 60 °C (bath temperature) for 30 min, and filtered hot, to yield N-benzylideneaniline (1.7 g) which had m.p. 46—48 °C (from diethyl ether) (lit.,[18] 48—49 °C).

Action of Benzonitrile on N-*Benzylideneaniline.*—Benzonitrile (0.17 g) and *N*-benzylideneaniline (0.31 g) were heated together at 190 °C (bath temperature) for 20 min. The starting materials were recovered unchanged. The experiment was repeated with the addition of 3,6-diphenyl-*s*-tetrazine (**1**) (0.39 g) to the mixture, with the same result.

Crystal Data.—$C_{23}H_{20}N_2$, M = 324.4. Monoclinic, space group $P2_1/c$, a = 5.749(4), b = 14.762(10), c = 21.854(17) Å, β = 109.24(10)°, V = 1 751 Å^3, Z = 4, D_c = 1.230 g cm^{-3}; Cu-K_α radiation, λ = 1.5418 Å, μ = 4.8 cm^{-1}.

Intensity data were measured by use of a microdensitometer (S.E.R.C. service, Daresbury Laboratory) from multi-film Weissenberg photographs of layers *h*0—5*l* and 0—5*kl*. The intensities decreased markedly at higher θ and only 1 004 unique data were above background (merging R 0.045). All non-hydrogen atoms except for four phenyl carbon atoms were located from an *E*-map generated after the inclusion of 2 618 unobserved reflections ($|F| = 0.2|F_o|_{min}$). The completion of the structure and subsequent refinement (observed data only) were conventional. As not all H atoms could be clearly distinguished in a difference synthesis calculated towards the end of full-matrix refinement, the H atoms were all included at calculated positions in the last cycles. Convergence was reached at R 0.088, w_R ($=[\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$) 0.097, 164 parameters, with unit weights for all data and with anisotropic thermal parameters for the core atoms N(1,3), C(2,4—10). The final difference synthesis was featureless (max. 0.34, min. −0.32 e Å^{-3}). The SHELX-76 program[19] was used in all calculations. Atomic co-ordinates are given in Table 1, and bond lengths and angles in Table 2. Thermal parameters are in Supplementary Publication No. SUP 56376 (3 pp.).* Structure factors may be obtained from the editorial office on request.

Table 2. Bond lengths (Å) inter-bond angles (°)

C(2)–N(1)	1.313(9)	C(12)–C(11)	1.472(15)
C(9)–N(1)	1.366(11)	C(13)–C(11)	1.516(16)
N(3)–C(2)	1.382(9)	C(15)–C(14)	1.386(11)
C(14)–C(2)	1.470(11)	C(19)–C(14)	1.371(11)
C(4)–N(3)	1.309(10)	C(16)–C(15)	1.378(13)
C(10)–C(4)	1.425(11)	C(17)–C(16)	1.376(13)
C(20)–C(4)	1.487(10)	C(18)–C(17)	1.370(12)
C(6)–C(5)	1.370(11)	C(19)–C(18)	1.382(12)
C(10)–C(5)	1.409(12)	C(21)–C(20)	1.375(10)
C(7)–C(6)	1.405(12)	C(25)–C(20)	1.367(11)
C(11)–C(6)	1.530(13)	C(22)–C(21)	1.408(12)
C(8)–C(7)	1.359(13)	C(23)–C(22)	1.364(11)
C(9)–C(8)	1.407(11)	C(24)–C(23)	1.360(11)
C(10)–C(9)	1.407(10)	C(25)–C(24)	1.407(12)

C(9)–N(1)–C(2)	116.9(7)	C(12)–C(11)–C(6)	113.7(10)
N(3)–C(2)–N(1)	125.2(8)	C(13)–C(11)–C(6)	109.1(4)
C(14)–C(2)–N(1)	118.5(7)	C(13)–C(11)–C(12)	106.4(11)
C(14)–C(2)–N(3)	116.2(8)	C(15)–C(14)–C(2)	119.5(8)
C(4)–N(3)–C(2)	118.1(8)	C(19)–C(14)–C(2)	122.0(8)
C(10)–C(4)–N(3)	121.7(7)	C(19)–C(14)–C(15)	118.5(9)
C(20)–C(4)–N(3)	116.3(7)	C(16)–C(15)–C(14)	119.4(10)
C(20)–C(4)–C(10)	122.0(8)	C(17)–C(16)–C(15)	121.9(11)
C(10)–C(5)–C(6)	120.8(8)	C(18)–C(17)–C(16)	118.5(11)
C(7)–C(6)–C(5)	118.7(9)	C(19)–C(18)–C(17)	119.9(10)
C(11)–C(6)–C(5)	119.0(9)	C(18)–C(19)–C(14)	121.7(9)
C(11)–C(6)–C(7)	122.2(9)	C(21)–C(20)–C(4)	120.0(8)
C(8)–C(7)–C(6)	121.8(9)	C(25)–C(20)–C(4)	120.7(8)
C(9)–C(8)–C(7)	120.2(9)	C(25)–C(20)–C(21)	119.3(8)
C(8)–C(9)–N(1)	119.0(8)	C(22)–C(21)–C(20)	120.5(9)
C(10)–C(9)–N(1)	122.2(8)	C(23)–C(22)–C(21)	119.1(9)
C(10)–C(9)–C(8)	118.7(9)	C(24)–C(23)–C(22)	121.1(9)
C(5)–C(10)–C(4)	124.6(8)	C(25)–C(24)–C(23)	119.6(10)
C(9)–C(10)–C(4)	115.7(9)	C(24)–C(25)–C(20)	120.4(9)
C(9)–C(10)–C(5)	119.5(8)		

* For details of the Supplementary Publications Scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

References

1 D. Hunter and D. G. Neilson, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2779.
2 A. Neugebauer, C. Krieger, H. Fischer, and R. Siegel, *Chem. Ber.*, 1983, **116**, 2261.
3 L. Birkofer, A. Ritter, and P. Richter, *Chem. Ber.*, 1963, **96**, 2750.
4 R. Huisgen, J. Sauer, and M. Seidel, *Justus Liebigs. Ann. Chem.*, 1962, **654**, 146.
5 R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Justus Liebigs. Ann. Chem.*, 1962, **653**, 105.
6 W. Fliege, R. Grashey, and R. Huisgen, *Chem. Ber.*, 1984, **117**, 1194.
7 A. Pinner and N. Caro, *Ber. Dtsch. Chem. Ges.*, 1894, **27**, 3273.
8 D. Hunter, D. G. Neilson, and T. J. R. Weakley, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1165.
9 D. Hunter and D. G. Neilson, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1081.
10 C. Huiszoon, *Acta Crystallogr., Sect. B*, 1976, **32**, 998.
11 D. Hunter and D. G. Neilson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1601.
12 E. Steininger, *Monatsh. Chem.*, 1966, **97**, 1195.
13 O. P. Shvaika and V. I. Fomenko, *Zh. Org. Khim.*, 1974, **10**, 377.
14 O. Jacobsen, *Ber. Dtsch. Chem. Ges.*, 1879, **12**, 429.
15 Tchitchibabine, S. Elgasine, and V. Lengold, *Bull. Soc. Chim. Fr.*, 1928, **43**, 238.
16 H. Meerwein, P. Laasch, R. Mersch, and J. Nentwig, *Chem. Ber.*, 1956, **89**, 224.
17 H. Wolchowe, *Monatsh. Chem.*, 1917, **37**, 473.
18 F. Tiemann and K. Piest, *Ber. Dtsch. Chem. Ges.*, 1882, **15**, 2028.
19 G. M. Sheldrick, SHELX-76 program for Crystal Structure Determination, Cambridge University, 1975.

Received 29th April 1985; *Paper* 5/701