The Reactions of Hydrazones and Related Compounds with Strong Bases. Part III.[1] 1,2,4-Triazoles, 1,2,4-Triazines, and 1,3,5-Triazines from Aromatic Aldehyde Azines [2]

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The reactions of aromatic aldehyde azines in boiling toluene with potassium t-butoxide furnished 3,5-diaryl-1,2,4 triazoles (2), trisubstituted 1,2,4-triazoles (3), 3,5,6-triaryl-1,2,4-triazines (5), (6), and (8), 2,4,6-triaryl-1,3,5-triazines (9), 2,4,5-triarylimidazoles (10), 3,4,5-triarylpyrazoles (11), benzonitriles, and other products. Mechanisms were studied by identifying products from the 'mixed' azine (13b; R = H) and by ^{14}C tracer methods. Application of the reaction to ketone azines (13; R = Ar) gave Wolff–Kishner products.

IN continuation of our studies of the reactions of hydrazones and related compounds with strong bases in aprotic solvents,[1] we have investigated the behaviour of aromatic aldehyde azines under these conditions, and now report the products isolated and discuss the mechanisms of the reactions.

Identification of Products.—Treatment of the azines (1) derived from benzaldehyde and from *m*- and *p*-methoxybenzaldehyde with potassium t-butoxide (1—2 mol. equiv.) in boiling toluene for 40 h in the absence of oxygen resulted in complete consumption of the azine. In each case, a number of products were isolated and identified (Table 1).

TABLE 1

Products from reaction of aldehyde azines (1) with potassium t-butoxide (1.4—1.9 mol. equiv.) in toluene at 110 °C for 40 h

	Yields (%) [a] from azine		
Products	(1a) [b]	(1b)	(1c)
1,2,4-Triazoles (2)	15	41	4
1,2,4-Triazoles (3)	18	13	22
1,2,4-Triazines (5)	1 [c]		
1,3,5-Triazines (9)	1	7	4
Imidazoles (10)	22	4	
Pyrazoles (11)	2	2	
Benzoic acids	18	26	
Benzonitriles		13	15

[a] Calculated assuming that azine (2 mol) gives triazoles, triazines, and pyrazoles (1 mol), that azine (3 mol) gives imidazoles (1 mol), and that azine (1 mol) gives acids and nitriles (1 mol). [b] The dihydro-1,2,4-triazine (6a) (7%) and the tetrahydro-1,2,4-triazine (8) (21%) were also isolated. [c] When the reaction was carried out for 5 h, the triazine (5a) was obtained in greater yield (21%); the lower yield after 40 h apparently is due to conversion of the triazine into N-benzoyl-1,2-diphenylvinylamine and other products.

1,2,4-Triazoles were major products, comprising acidic 3,5-diaryl derivatives (2) (4—41%) and trisubstituted compounds (3) (13—22%) isolated from neutral fractions. The trisubstituted compound derived from benzaldehyde azine (1a) was shown to be an N-benzyl derivative [(3a) or (4)] by a two-proton n.m.r. singlet at τ 4.59 (C*H*₂Ph), by its conversion into 3,5-diphenyl-1,2,4-triazole (2a) with sodium in liquid ammonia, and by its preparation through benzylation of the triazole (2a). The n.m.r. spectra of the benzyltriazoles are consistent with the presence of a 1-substituent as in the unsymmetrically substituted compounds (3) rather than a

4-substituent as in the symmetrical isomers (4). Thus, only two aryl protons are deshielded relative to other aryl protons, indicating that the 3-aryl group is coplanar with the heterocyclic ring whereas the 5-aryl group is

ArCH=N—N=CHAr
(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)

R\C=N—N=CPh₂
(13)

(PhCH=N)₂CHPh
(14)
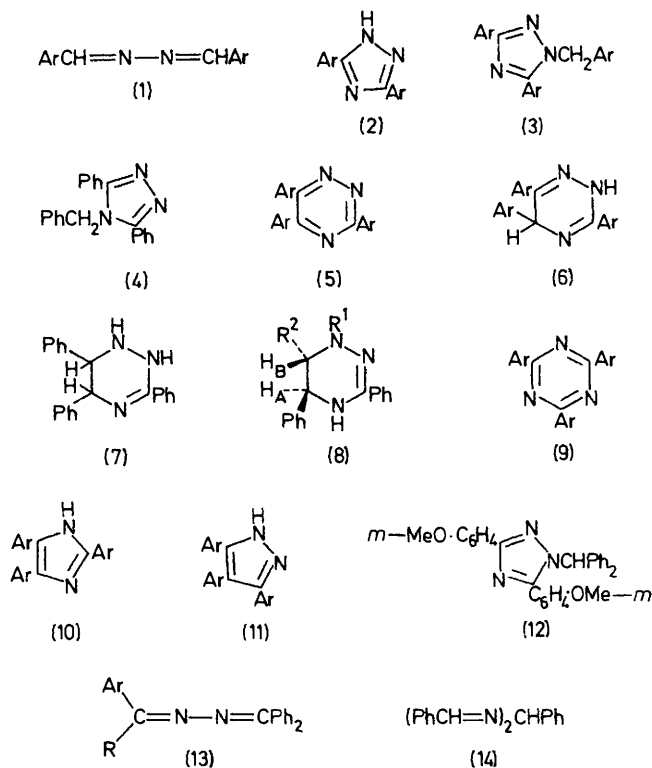
a; Ar = Ph
b; Ar = *m*—MeO·C₆H₄
c; Ar = *p*—MeO·C₆H₄

subject to steric hindrance by the 1-substituent; the non-equivalence of the three aryl rings in the triazole (3b) was further indicated by distinct three-proton singlets at τ 6.15, 6.27, and 6.38 (OMe).

3,4,6-Triphenyl-1,2,4-triazine (5a) was obtained from benzaldehyde azine (Table 1). A colourless, basic compound, $C_{21}H_{17}N_3$, was also isolated from this reaction, and was apparently a dihydro-3,5,6-triphenyl-1,2,4-triazine, since treatment with palladium in boiling

[1] Part II, M. F. Grundon and M. D. Scott, *J. Chem. Soc.*, 1964, 5674.

[2] Preliminary communication, J. T. A. Boyle and M. F. Grundon, *Chem. Comm.*, 1967, 1137.

xylene gave 3,5,6-triphenyl-1,2,4-triazine. The dihydro-derivative was identical with the compound obtained by Metze and Scherowsky [3] from the triazine with zinc and acetic acid, but in our hands this method was unsatisfactory and gave 2,4,5-triphenylimidazole (10a) as principal product; reduction with sodium borohydride in boiling propan-2-ol, however, afforded the dihydro-derivative quantitatively. Since the compound was too insoluble in neutral solvents for the n.m.r. spectrum to be determined, the more soluble m-methoxyphenyl derivative was prepared by reduction with borohydride of the corresponding triazine (5b), and the n.m.r. spectra of solutions in [^{2}H]chloroform, [^{2}H$_6$]dimethyl sulphoxide, and acetone were examined; because CH,NH-coupling was not observed, formulation of the compounds as 2,5-dihydro-derivatives (6a and b) is preferred.

Another basic compound isolated from the reaction of benzaldehyde azine with potassium t-butoxide apparently was a tetrahydro-3,5,6-triphenyl-1,2,4-triazine (7) or (8; R^1 = H, R^2 = Ph). The mass spectrum showed a molecular ion peak at m/e 313 and i.r. absorption occurred at 3 200 (NH) and 1 610 cm^{-1} (C=N). In the n.m.r. spectrum (CDCl$_3$), two broad one-proton singlets appeared at τ 4.7 and at 5.0 (NH) and two one-proton coupled doublets at τ 5.37 (H$_A$) and at 6.25 (H$_B$) (J 7.5 Hz, CHPh); the CH chemical shifts and the coupling constant are close to those reported for the analogous 1,4,5,6-tetrahydrotriazine (8; R^1 = R^2 = Me),[4] after allowance is made for the presence of a phenyl rather than a methyl substituent at position 6, and this suggests that our compound is also a 1,4,5,6-tetrahydro-derivative (8; R^1 = H, R^2 = Ph). The product gave a mono-acetyl derivative, formulated as (8; R^1 = Ac, R^2 = Ph) since in the n.m.r. spectrum the H$_B$ resonance had shifted downfield to τ 4.41 (J 5.3 Hz) whereas the H$_A$ proton showed a chemical shift at τ 5.13 similar to that in the parent triazine (8; R^1 = H, R^2 = Ph).

Other heterocyclic compounds identified from the reactions of the azines with base included the 1,3,5-triazines (9a—c), the 2,4,5-triarylimidazoles (10a and b), and the 3,4,5-triarylpyrazoles (11a and b) (Table 1). The corresponding benzonitriles were obtained from the azines (1b and c), benzoic acid and m-methoxybenzoic acid were isolated from the reactions of benzaldehyde azine and of m-methoxybenzaldehyde azine, respectively, and benzaldehyde azine gave a small yield of trans-stilbene.

Mechanisms.—The recognition of 1-benzyl-1,2,4-triazoles (3) and 1,2,4-triazines (5), (6), and (8) as principal products of the reaction suggested that Ar–N fragments were formed and added subsequently to azine molecules. In order to assist in the interpretation of the reactions, the behaviour of the 'mixed' azine (13b; R = H), prepared from m-methoxybenzaldehyde and benzophenone hydrazone, was studied. The products (Experimental section) included the diphenylmethyl-1,2,4-triazole (12) (12%); its structure was established by the n.m.r. spectrum, which showed a one-proton singlet at τ 3.27 (CHPh$_2$) and three-proton singlets at τ 6.15 and

at 6.25 (OMe), and by its preparation through alkylation of 3,5-bis-(m-methoxyphenyl)-1,2,4-triazole (2b). The isolation of the triazole (12) supports the conclusion that an intact azine molecule can take part in the formation of heterocyclic products.

The formation of benzonitriles and benzoic acids in the reactions suggested that Ar–N units for addition to azine were provided by the elimination reaction (i).
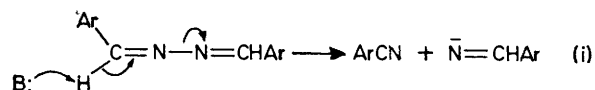
The imines probably are responsible for the isolation of benzoic acids through hydrolysis to aldehydes and subsequent oxidation. Formation of the acids from nitriles can be only a minor route, since benzonitrile was mainly unaffected when submitted to the reaction conditions, and in the tracer experiments with benzo-[^{14}C]nitrile (Experimental section) the benzoic acid obtained contained only a small proportion of the initial activity.

Similarly, m-methoxybenzonitrile was formed from the 'mixed' azine (13b; R = H); benzophenone (8%) was also isolated, mainly from the acid-soluble fraction, indicating that diphenylmethyleneamine was the primary product of elimination in this case. The imidazoles (10) may also arise from amines produced in an initial elimination reaction, since $\alpha\alpha$-bisbenzylideneamino-toluene (14), a known product from benzylideneamine, is converted with strong base into 2,4,5-triphenyl-imidazole (10a).[5]

In order to decide whether benzonitriles could be intermediates in the formation of the triazoles (2) and (3), the triazines (5), (6a), and (8; R^1 = H, R^2 = Ph), and other products, ^{14}C-labelled benzonitrile was added in the reaction between benzaldehyde azine and potassium t-butoxide. In duplicate experiments, only
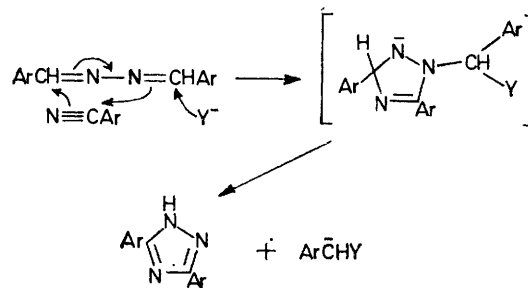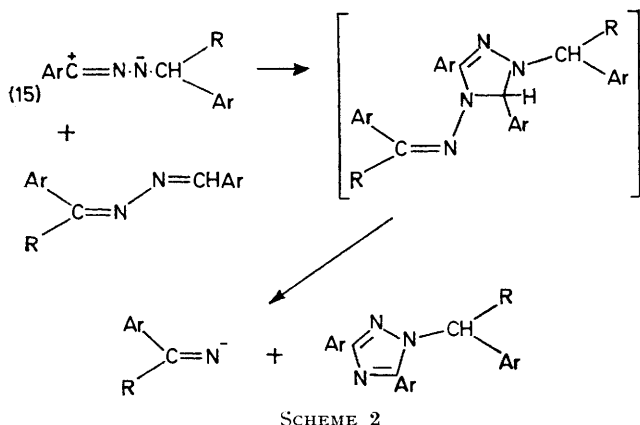

Scheme 1

3,5-diphenyl-1,2,4-triazole (2a) was labelled substantially (Experimental section), and we propose that one route to the triazoles (2) involves attack of a nucleophile on an azine molecule concerted with addition of nitrile (Scheme

[3] R. Metze and G. Scherowsky, *Chem. Ber.*, 1959, **92**, 2487.
[4] D. L. Trepanier, E. R. Wagner, G. Harris, and A. D. Rudzik, *J. Medicin. Chem.*, 1966, **9**, 881; D. L. Trepanier, J. E. Richman, and A. D. Rudzik, *ibid.*, 1967, **10**, 228.
[5] A. Spassov and S. Robev, *Chem. Ber.*, 1965, **98**, 928.

1). The nucleophile (Y⁻) may be the anion ArCH=N⁻ or ArC̄=N-N=CHAr, which would provide good leaving groups for subsequent elimination, or less likely the t-butoxide ion. Since debenzylation of the *N*-benzyltriazole (3a) occurs slowly under the reaction

SCHEME 2

conditions, some triazole (2) must be formed in this way, and an additional pathway not requiring participation of nitrile may involve dimerization of azine promoted by a nucleophile, followed by elimination of two substituents (Scheme 1; ArCH=N-N=CHAr in place of ArCN).

We suggest that the trisubstituted triazoles (3) and (12) are formed by 1,3-dipolar cycloaddition of species (15) to a second molecule of azine, analogous to reactions of diphenylnitrilimine;[6] subsequent elimination from a dihydrotriazole than furnishes imines or diphenylmethyleneamine (Scheme 2).

There is less evidence on which to base mechanisms for the formation of the 1,2,4- and 1,3,5-triazines, although the tracer experiments show that principal routes do not involve benzonitriles. When the 2,5-dihydrotriazine (6a) was refluxed in toluene with potassium t-butoxide (1—4 mol. equiv.) rearrangement occurred to give a mixture of the 1,3,5-triazine (9a) and its 1,2-dihydro-derivative, but when less base was used the 1,2,4-triazine (5a) was obtained as well as the 1,3,5-isomer. We conclude that in the reaction of benzaldehyde azines with base the triazines formed initially probably are the 2,5-dihydro-1,2,4-triazines, which subsequently are converted into the triazines (5). A mechanism involving 1,4-addition of an azine molecule to the C=N bond of another is proposed (Scheme 3). The tetrahydro-1,2,4-triazine (8; R¹ = H, R² = Ph) may arise by addition of the anion of benzylideneamine to benzaldehyde azine.

Since the dihydro-1,2,4-triazine (6a) is converted with potassium t-butoxide into a 1,3,5-triazine (9a) (see before), this rearrangement may account for the isolation of 1,3,5-triazines in the reactions of azines (1a—c) with base (Table 1); that the 1,3,5-triazines do not arise by

[6] R. Huisgen, R. Grashey, E. Aufderhaar, and R. Kunz, *Chem. Ber.*, 1965, **98**, 642.
[7] H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, 1960, **82**, 5865.

trimerization of benzonitriles was demonstrated when benzamide was the only product obtained by treating benzonitrile with potassium t-butoxide in the usual way.

trans-Stilbene was a minor product of the reaction of benzaldehyde azine with base, and probably arises by a thermal process, shown previously to proceed by an ionic chain mechanism catalysed by diazo(phenyl)-methane.[7] The latter compound apparently is not involved in the formation of heterocyclic compounds in our reactions, since triazines and 1,2,4-triazoles were not detected in the reactions of aromatic aldehyde azines with base in the presence of phenyldiazo(phenyl)-methane.[8]

Reactions of Ketone Azines.—In the reaction of benzophenone *m*-methoxybenzylidenehydrazone (13b; R = H) with base, the isolation of benzophenone azine and 3,4-bis-(*m*-methoxyphenyl)-1,2,4-triazole indicated that equilibration of the 'mixed' azine had occurred. We decided, therefore, to study the reactions of ketone azines with strong bases in aprotic solvents. Under our usual conditions, benzophenone azine (13a; R = Ph) (66%) was recovered, and diphenylmethane (13%) and tetraphenylethylene (2%) were isolated, with the liberation of nitrogen; in boiling xylene diphenylmethane (30%) was formed. The 'mixed' ketone azine [13b; R = C₆H₄(*m*-OMe)] reacted faster with base and afforded *p*-benzylanisole (97%) and diphenylmethane (50%). These are not the expected products of thermal reactions, which give nitriles and imines,[9] and we suggest

SCHEME 3
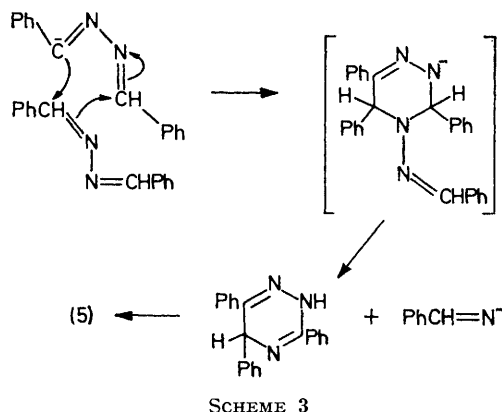
that diarylmethanes are formed by addition of t-butoxide anion to the ketone azine to give azo-derivatives, followed by homolytic cleavage of C-N bonds.

EXPERIMENTAL

N.m.r. spectra were determined with a Varian HR-100 spectrometer (tetramethylsilane as internal standard) and mass spectra with an A.E.I. MS 902 instrument. Radioactivity was measured with an Ekeo scintillation counter Nb64B, by use of a diphenyloxazole–toluene phosphor. Alumina refers to Spence grade H and light petroleum to the fraction of b.p. 40—60°.

Reaction of Benzaldehyde Azine (1a) *with Potassium t-Butoxide.*—A solution of benzaldehyde azine (10 g) and

[8] M. F. Grundon and E. A. Khan, unpublished work.
[9] S. S. Hirsch, *J. Org. Chem.*, 1967, **32**, 2433; N. P. Buu-Hoï and G. Saint-Ruf, *Bull. Soc. chim. France*, 1970, 343.

potassium t-butoxide (11.5 g) in toluene (500 ml) was refluxed in nitrogen for 40 h, water was added, and the two layers were separated. Acidification of the aqueous solution, extraction with chloroform, and heating the product with water gave 3,5-diphenyl-1,2,4-triazole (2a) as a solid (0.78 g), affording plates, m.p. 193° (from aqueous ethanol) (lit.,[10] m.p. 190°) (Found: C, 75.5; H, 4.8; N, 18.8. Calc. for $C_{14}H_{11}N_3$: C, 76.0; H, 5.0; N, 19.0%), identical (mixed m.p. and i.r.) with an authentic sample. Benzoic acid (0.67 g), m.p. and mixed m.p. 115—121°, was obtained from the aqueous solution.

The toluene solution, when shaken with aqueous hydrochloric acid, gave a precipitate, which, when extracted with hot ethanol, left 2,5-dihydro-3,5,6-triphenyl-1,2,4-triazine (6a) (0.34 g), m.p. 243° (lit.,[3] 239°) (needles from benzene–chloroform) (Found: C, 80.6; H, 5.4; N, 13.4. Calc. for $C_{21}H_{17}N_3$: C, 81.0; H, 5.5; N, 13.5%), identical (i.r. spectrum) with an authentic sample. Evaporation of the ethanolic solution and trituration of the residue with benzene gave 1,4,5,6-*tetrahydro*-3,5,6-*triphenyl*-1,2,4-*triazine monohydrochloride* (1.69 g), indefinite m.p. 225—255° (decomp.) (prisms from ethanol), $\nu_{max.}$ 3 100, 2 900, and 2 800 cm^{-1} (NH and NH$^+$) (Found: C, 72.1; H, 5.7; N, 12.0. $C_{21}H_{20}ClN_3$ requires C, 72.0; H, 5.7; N, 12.0%). The benzene-soluble fraction was chromatographed on alumina. Elution with ether gave more dihydrotriazine (6a) (0.2 g), and elution with ether–acetone (1 : 1) furnished 2,4,5-triphenylimidazole (0.56 g), m.p. 255—265° (lit.,[11] 272°) (needles from ethanol), identified by comparison of the i.r. spectrum with that of an authentic sample.

Evaporation of the toluene solution and extraction of the residue with benzene gave 3,4,5-triphenylpyrazole (11) (0.1 g), m.p. 268° (lit.,[12] 267°) (needles from ethanol) (Found: C, 84.6; H, 5.3; N, 9.3. Calc. for $C_{21}H_{16}N_2$: C, 85.1; H, 5.4; N, 9.5%), identical (mixed m.p. and i.r. spectrum) with an authentic sample. The benzene-soluble fraction was chromatographed on alumina. Elution with light petroleum gave *trans*-stilbene (0.13 g), m.p. 117—122°, and elution with light petroleum containing increasing proportions of ether gave, successively, 2,4,6-triphenyl-1,3,5-triazine (9a) (0.06 g), m.p. 235° (lit.,[13] 232°) (needles from methanol); 1-benzyl-3,5-diphenyl-1,2,4-triazole (3a) (1.32 g), m.p. 96—97° (prisms from ethanol); and 3,5,6-triphenyl-1,2,4-triazine (5a) (0.1 g), m.p. 146—147° (lit.,[14] 145—146°) (yellow needles from ethanol); these three compounds were identified by comparison (i.r. spectra and mixed m.p.) with authentic samples.

3,5,6-*Tris*-(m-*methoxyphenyl*)-1,2,4-*triazine* (5b).—The method of Laakso et al.[14] gave the *triazine* (83%), m.p. 93—94° (yellow needles from ethanol), τ (CDCl$_3$) 6.08 (3 H, s, OMe in 3-aryl group) and 6.23 (3 H, s) and 6.28 (3 H, s) (other OMe) (Found: C, 71.5; H, 5.2; N, 10.8. $C_{24}H_{21}N_3O_3$ requires C, 72.2; H, 5.3; N, 10.5%).

2,5-*Dihydro*-3,5,6-*triaryl*-1,2,4-*triazines* (6).—A solution of the triazine (5b) (1.93 g) and sodium borohydride (1 g) in propan-2-ol (200 ml) was refluxed for 4 h and added to water. Extraction with chloroform afforded 2,5-*dihydro*-3,5,6-*tris*-(m-*methoxyphenyl*)-1,2,4-*triazine* (1.57 g, 81%), m.p. 148—150° (needles from ethanol), τ (CDCl$_3$) 4.08 (1 H, s, CH), 6.23 (6 H, s, 2 OMe), and 6.28 (3 H, s, OMe),

τ [(CD$_3$)$_2$SO] 4.08 (1 H, s, CH), 6.21 (3 H, s), 6.24 (3 H, s), and 6.32 (3 H, s), τ (Me$_2$CO) 3.98 (1 H, s, CH), 6.10 (3 H, s), 6.13 (3 H, s), and 6.21 (3 H, s) (Found: C, 72.4; H, 5.8; N, 10.7. $C_{24}H_{23}N_3O_3$ requires C, 71.8; H, 5.8; N, 10.5%).

3,5,6-Triphenyl-1,2,4-triazine was converted similarly into the 2,5-dihydro-derivative (100%), m.p. 243°; reaction of the triazine with zinc, acetic acid, and ethanol gave 2,4,5-triphenylimidazole (47%), m.p. 270—273°, identical with an authentic sample.

The dihydrotriazine (6a) (197 mg) in 1,2,4-trimethylbenzene was refluxed with 10% palladium–charcoal (50 mg) for 6 h, and gave 3,5,6-triphenyl-1,2,4-triazine (180 mg, 90%), m.p. 145° (yellow needles from ethanol).

Reaction of 2,5-Dihydro-3,5,6-triphenyl-1,2,4-triazine with Potassium t-Butoxide.—(a) Reaction of the dihydrotriazine (6a) (1.9 g) with potassium t-butoxide (2.0 g) in the usual way gave a product (1.19 g), m.p. 150—180°, τ 1.19, 1.97, 2.33—2.90, and 3.72 (2,4,6-triphenyl-1,3,5-triazine, τ 1.19 and 2.32—2.48; 1,2-dihydro-2,4,6-triphenyl-1,3,5-triazine,[16] τ 1.96, 2.50, and 3.75). Heating the product at 190—200° for 10 min gave 2,4,6-triphenyl-1,3,5-triazine, m.p. 234—235° (needles from ethanol).

(b) The dihydrotriazine (2.0 g) and potassium t-butoxide (0.6 g) gave a yellow solid (0.59 g) which on trituration with hot ethanol furnished 2,4,6-triphenyl-1,3,5-triazine (86 mg), m.p. 222—232°. Concentration of the ethanolic solution gave 3,5,6-triphenyl-1,2,4-triazine (157 mg), m.p. 140—144°.

1,4,5,6-*Tetrahydro*-3,5,6-*triphenyl*-1,2,4-*triazine* (8; R^1 = H, R^2 = Ph) *and its Monoacetyl Derivative* (8; R^1 = Ac, R^2 = Ph).—Addition of aqueous sodium hydroxide to a solution of the hydrochloride (see before) in hot water gave the *tetrahydrotriazine*, m.p. 160—162°, m/e 313 (M^+, 35%), 209 ($M^+ - C_7H_6N$, 7%), 180 ($C_8H_{12}^+$, 11%), 106 ($C_7H_8N^+$, 100%), 105 ($C_7H_7N^+$, 54%), 104 ($C_7H_6N^+$, 95%), and 103 ($C_8H_{12}^+ - C_6H_5$, 7%) (Found: C, 80.9; H, 5.9; N, 13.1. $C_{21}H_{19}N_2$ requires C, 80.5; H, 6.1; N, 13.4%).

The amine hydrochloride and acetic anhydride were heated at 100 °C for 2 h to give the 1-*acetyltriazine*, m.p. 212° (needles from di-isopropyl ether–methanol–light petroleum), $\nu_{max.}$ 3 200 (NH) and 1 630 cm^{-1} (NCO) (Found: C, 77.9; H, 5.7; N, 12.0. $C_{23}H_{21}N_3O$ requires C, 77.7; H, 6.0; N, 11.8%).

1-*Benzyl*-3,5-*diphenyl*-1,2,4-*triazole* (3a).—A solution of 3,5-diphenyl-1,2,4-triazole (300 mg), sodium (50 mg), and benzyl chloride (300 mg) in ethanol was refluxed for 30 min, chloroform was added, and the solution was washed with water. The chloroform solution was evaporated, and the residue was chromatographed on alumina. Elution with benzene gave the *benzyltriazole*, m.p. 96—97° (prisms from ethanol) (Found: C, 80.6; H, 5.4; N, 13.0. $C_{21}H_{17}N_3$ requires C, 81.0; H, 5.5; N, 13.5%).

Sodium was added to a solution of the benzyltriazole (357 mg) in liquid ammonia (25 ml), and after 5 min ammonium chloride was added. Evaporation, addition of aqueous sulphuric acid, and extraction with chloroform gave 3,5-diphenyl-1,2,4-triazole (169 mg, 66%), m.p. 190—192° (plates from aqueous ethanol).

3,5-*Bis*-(m-*methoxyphenyl*)-1,2,4-*triazole* (2b).—A solution of m-methoxybenzohydrazide (6.6 g) and toluene-p-sulphonic acid (6.8 g) in hot ethanol (10 ml) was allowed to cool.

[10] K. T. Potts, J. Chem. Soc., 1954, 3463.
[11] D. Davidson, M. Weiss, and M. Jelling, J. Org. Chem., 1937, 2, 319.
[12] W. E. Parham and W. R. Hasek, J. Amer. Chem. Soc., 1954, 76, 800.
[13] A. H. Cook and D. G. Jones, J. Chem. Soc., 1941, 278.
[14] P. V. Laakso, R. Robinson, and H. P. Vandrewala, Tetrahedron, 1957, 1, 110.
[15] J. Robin, Ann. Chim. (France), 1921, 16, 117.
[16] H. L. Nyquist, J. Org. Chem., 1966, 31, 784.

Addition of ether precipitated m-*methoxybenzohydrazide* *toluene*-p-*sulphonate* (9.6 g), m.p. 115—117° (needles from ether–propan-2-ol) (Found: C, 53.3; H, 5.2; N, 8.5. $C_{15}H_{18}N_2O_5S$ requires C, 53.3; H, 5.4; N, 8.3%).

A mixture of the sulphonate (7.9 g) and m-methoxy-benzonitrile (3.0 g) was heated at 200 °C for 2 h. The product in aqueous sodium hydroxide was acidified to give a precipitate of the *triazole* (1.6 g), m.p. 189—191° (needles from ethanol) (Found: C, 67.9; H, 5.5; N, 15.1. $C_{16}H_{15}N_3O_2$ requires C, 68.3; H, 5.4; N, 14.9%). Addition of water to a solution of the triazole in ethanol gave a solid, m.p. 135—145°, separating from ethanol in needles, m.p. 158—159°. The two forms had slightly different i.r. spectra in the NH stretching region.

1-m-*Methoxybenzyl*-3,5-*bis*-(m-*methoxyphenyl*)-1,2,4-*tri-azole* (3b).—A mixture of 3,5-bis-(m-methoxyphenyl)-1,2,4-triazole (470 mg), m-methoxybenzyl chloride (530 mg), anhydrous sodium carbonate (200 mg), and xylene (10 ml) was refluxed for 24 h. The product was obtained with chloroform and chromatographed on alumina. Elution with benzene–ether (2 : 1) gave the benzyltriazole (186 mg, 28%), m.p. 108—109° (needles from di-isopropyl ether), τ (CDCl₃) 2.14—2.32 (2 H, m), 2.54—3.30 (10 H, m), 4.60 (2 H, s, CH₂), 6.15 (3 H, s, OMe in 3-aryl group), 6.27 (3 H, s, OMe in 5-aryl group), and 6.28 (3 H, s, OMe in benzyl group). A satisfactory elemental analysis was not obtained.

Reaction of m-*Methoxybenzaldehyde Azine* (1b) *with Potassium t-Butoxide*.—A solution of m-methoxybenz-aldehyde azine and potassium t-butoxide in toluene was refluxed as described for the reaction of benzaldehyde azine and by a similar work-up procedure the following compounds were isolated: 3,5-bis-(m-methoxyphenyl)-1,2,4-triazole (2b), 1-m-methoxybenzyl-3,5-bis-(m-methoxy-phenyl)-1,2,4-triazole (3b), 2,4,5-tris-(m-methoxyphenyl)-imidazole (10b), m-methoxybenzoic acid, and m-methoxy-benzonitrile. These compounds were identified by comparison with authentic samples, and yields are given in Table 1.

A neutral product, m.p. 175° (needles from ethanol-benzene) (Found: C, 72.0; H, 5.3; N, 10.8. $C_{24}H_{21}N_3O_3$ requires C, 72.2; H, 5.3; N, 10.5%) is probably 2,4,6-*tris*-(m-*methoxyphenyl*)-1,3,5-*triazine* (9b).

A neutral constituent, m.p. 165—166° (needles from ethanol), $v_{max.}$ 3 330 (NH) (Found: C, 75.0; H, 5.8; N, 7.3. $C_{24}H_{22}N_2O_3$ requires C, 74.6; H, 5.7; N, 7.3%) has an i.r. spectrum similar to that of the pyrazole (11a) and is probably 3,4,5-*tris*-(m-*methoxyphenyl*)*pyrazole* (11b).

2,4,5-*Tris*-(m-*methoxyphenyl*)*imidazole* (10b).—A solution of 3,3'-dimethoxybenzil (6.3 g), m-methoxybenzaldehyde (3 ml), and ammonium acetate (18 g) in acetic acid (140 ml) was refluxed for 2 h, added to water, and then extracted with chloroform. Shaking the extract with aqueous sodium hydroxide gave a precipitate of the *imidazole* (5.0 g, 56%), m.p. 186—187° (prisms from ethanol) (Found: C, 74.7; H, 5.8; N, 7.5. $C_{24}H_{22}N_2O_3$ requires C, 74.6; H, 5.7; N, 7.5%).

Reaction of p-*Methoxybenzaldehyde Azine* (1c) *with Potassium t-Butoxide*.—Reaction of p-methoxybenzaldehyde azine with potassium t-butoxide was carried out as described for benzaldehyde azine and by a similar work-up the following compounds were isolated: an acidic compound, m.p. 195—205°, $v_{max.}$ 3 200—2 400 cm⁻¹ (NH), probably 3,5-bis-(p-methoxyphenyl)-1,2,4-triazole (2c) (lit.,[5] m.p. 196—197°); 1-p-*methoxybenzyl*-3,5-*bis*-(p-*methoxy-phenyl*)-1,2,4-*triazole* (3c), m.p. 123—124° (prisms from

ethanol), τ (CDCl₃) 1.7—3.2 (12 H), 4.65 (2 H, s, CH₂), 6.17 (3 H, s), 6.23 (3 H, s), and 6.4 (3 H, s) (Found: C, 72.5; H, 5.5. $C_{24}H_{23}N_3O_3$ requires C, 71.9; H, 5.7%); 2,4,6-tris-(p-methoxyphenyl)-1,3,5-triazine (9c), m.p. 227° (lit.,[15] 224°) (Found: C, 71.4; H, 5.2; N, 10.5. Calc. for $C_{24}H_{21}N_3O_3$: C, 72.2; H, 5.3; N, 10.5%); and anisonitrile, identical (i.r. spectrum) with an authentic sample. Yields are given in Table 1.

Benzophenone m-*Methoxybenzylidenehydrazone* (13b; R = H).—m-Methoxybenzaldehyde (7.2 g) in ethanol (10 ml) was added slowly to a solution of benzophenone hydrazone (10 g) in ethanol (200 ml). Concentration gave the benzyl-idenehydrazone (15.1 g, 95%), m.p. 101—103°, τ (CDCl₃) 1.46 (1 H, s, CH=N), 2.20—3.12 (14 H), and 6.25 (3 H, s, OMe). A satisfactory analysis was not obtained.

Reaction of Benzophenone m-*Methoxybenzylidenehydrazone with Potassium t-Butoxide*.—The reaction was carried out as described for benzaldehyde azine. The acidic fraction contained m-methoxybenzoic acid (6%) and 3,5-bis-m-methoxyphenyl-1,2,4-triazole (31%). The acidic fraction after neutralisation, extraction into chloroform, and chromatography gave benzophenone (8%). Chromato-graphy of the neutral fraction on alumina furnished di-phenylmethane (10%), tetraphenylethylene (1%), m-methoxybenzonitrile (1%), benzophenone azine (26%), 1-m-methoxybenzyl-3,5-bis-(m-methoxyphenyl)-1,2,4-tri-azole (3b) (4%), 1-diphenylmethyl-3,5-bis-(m-methoxy-phenyl)-1,2,4-triazole (12) (18%), and 2,4,5-tris-(m-methoxyphenyl)imidazole (10b) (1%). All products were identified by comparison with authentic samples.

1-*Diphenylmethyl*-3,5-*bis*-(m-*methoxyphenyl*)-1,2,4-*triazole* (12).—A mixture of 3,5-bis-(m-methoxyphenyl)-1,2,4-tri-azole (250 mg), diphenylmethyl chloride (500 mg), an-hydrous sodium carbonate (200 mg), and xylene (10 ml) was refluxed for 24 h. The products, recovered with chloroform, gave the *diphenylmethyltriazole* (262 mg, 66%), m.p. 148—150° (needles from ethanol) (Found: C, 78.3; H, 5.8; N, 9.0. $C_{29}H_{25}N_3O_2$ requires C, 77.8; H, 5.6; N, 9.4%).

TABLE 2

Products from benzaldehyde azine with potassium
t-butoxide in the presence of benzo[¹⁴C]nitrile

Compound	(a) Yield[a]	(a) Activity[b]	(b) Yield[a]	(b) Activity[b]
(3a)	9	0.6[e]	5	0.2
(2a)	6	10.7	12	31.1
(5a)	6	0.04[d]		
(6a)	5	1.5	4	
(8; R¹ = H, R² = Ph)	7	0.7		
(10a)			5	1.3
(11a)	0.5	0.2	2	
(9a)	0.5	0.05	0.2	
Benzoic acid	15	1.8	14	2.2

[a] Calc. as (wt. of product × 100)/(wt. of azine). [b] Calc. as (total radioactivity of product × 100)/(total radioactivity of Ph¹⁴CN). [e] Unchanged after debenzylation and counting 3,5-diphenyl-1,2,4-triazole. [d] Counted as 2,4,5-triphenylimidazole, obtained by reaction with zinc and acetic acid.

Reaction of Benzaldehyde Azine with Potassium t-Butoxide in the Presence of Benzo[¹⁴C]*nitrile*.—Benzo[¹⁴C]nitrile (100—108 mg) was added to benzaldehyde azine (10 g) and potassium t-butoxide in refluxing toluene, and products were isolated in the usual way. The results in two experi-ments, (a) and (b) are in Table 2.

Reaction of Benzophenone Azine with Potassium t-Butoxide. —A solution of benzophenone azine (2.0 g) and potassium t-butoxide (2.4 g) in toluene (95 ml) was refluxed for 40 h in a flask attached to a gas burette; nitrogen (43 ml, 35%) was liberated. The toluene solution was washed with water and evaporated. Trituration of the residue with light petroleum gave unchanged azine (1.31 g, 66%). Chromatography of the light petroleum solution on alumina gave first diphenylmethane (238 mg, 13%), n_D^{20} 1.5730, and then tetraphenylethylene (34 mg, 2%), m.p. 170—190°. The products were identified by comparison (i.r. spectra) with authentic samples.

p-Methoxybenzophenone Diphenylmethylenehydrazone (13). —A solution of benzophenone hydrazone (6 g), *p*-methoxybenzophenone (6.3 g) and potassium hydroxide (27 g) in ethanol (90 ml) was refluxed for 20 min, then added to water, and the products were recovered with chloroform. Chromatography on alumina and elution with benzene furnished the *hydrazone* (1.75 g, 15%), m.p. 112—114° (yellow needles from methanol) (Found: C, 83.1; H, 6.0; N, 7.3. $C_{27}H_{22}N_2O$ requires C, 83.1; H, 5.7; N, 7.2%).

Reaction of p-Methoxybenzophenone Diphenylmethylenehydrazone with Potassium t-Butoxide.—The products, obtained in the usual way, were chromatographed on alumina. Elution with light petroleum–ether (20 : 1) gave diphenylmethane (50%) and then *p*-benzylanisole (97%), both identical (i.r. spectra) with authentic samples.