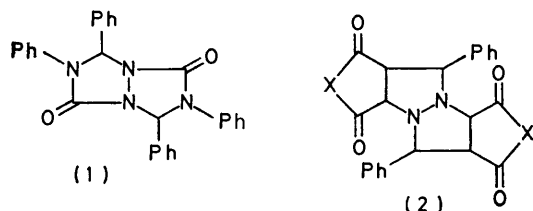


Syntheses of Heterocyclic Compounds. Part XXXI.¹ Triazolium Tetrafluoroborates from the Cycloaddition of Alkoxydiazonium Salts to Azines, Hydrazones, and Anils derived from Aromatic Aldehydes

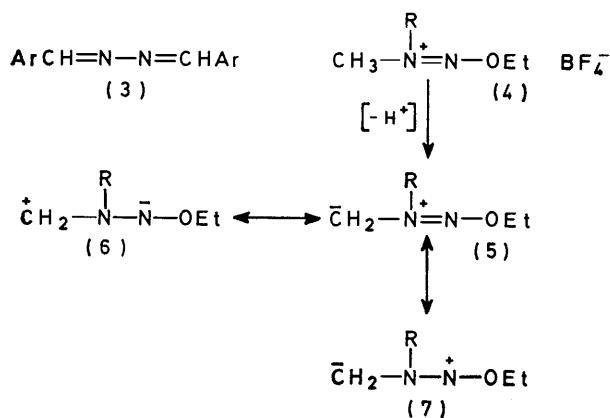
By **Suchet S. Mathur** and **Hans Suschitzky**,* The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire

The azomethine group in aromatic aldehyde azines and in *o*-dialkylamino-substituted aromatic Schiff's bases undergoes cycloaddition with alkoxydiazonium salts in dry dichloromethane to yield triazolium salts. Aromatic aldehyde hydrazones gave the triazolium salts (15) by a regiospecific cycloaddition, confirmed by an independent synthesis. Some reactions and physical data of these heterocycles and mechanistic aspects of their formation are discussed.

AZINES (3) are versatile intermediates for heterocyclic syntheses² owing to their ability to undergo 1,3-dipolar additions with a variety of dipolarophiles, *e.g.* phenyl isocyanate (1), maleic anhydride or maleimides (2; X = O or NR), and also intramolecular cycloadditions.³ By contrast their behaviour as dipolarophiles has been little explored; so far only the 1,3-dipoles diphenyl-nitrilimine⁴ and more recently epoxides⁵ have been reported to react with azines.



We describe here a study of the interaction of aldehyde azines and alkoxydiazonium salts.⁶ The best solvent for the reaction was dry dichloromethane, at room



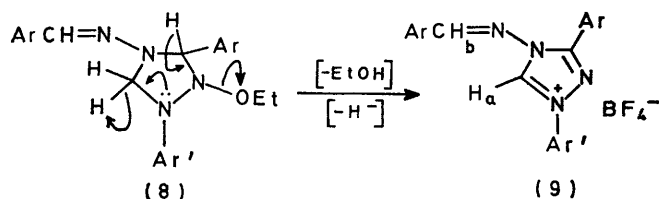
temperature. Other polar solvents, for instance nitromethane and dimethyl sulphoxide, gave lower yields and

¹ Part XXX, H. Suschitzky, B. J. Wakefield, and R. A. Whittaker, *J.C.S. Perkin I*, 1975, 2409.

² A. N. Kost and I. I. Grandberg, *Uspekhi Khim.*, 1959, **28**(8), 921 and references therein; D. Kolbah and D. Korunecv, *Methoden der Organischen Chemie*, 1967, **10**, 85; T. Wagner-Jauregg, *Ber.*, 1930, 3213; T. Wagner-Jauregg and L. Zirngibl, *Chimia (Switz.)*, 1968, **22**, 436; T. Wagner-Jauregg, L. Zirngibl, A. Demolis, H. Gunther, and S. W. Tam, *Helv. Chim. Acta*, 1969, **52**, 1672.

³ S. S. Mathur and H. Suschitzky, following paper.

at higher temperatures tarry products were obtained. The azines were sufficiently basic to cause deprotonation of the salt (4) to give a dipolar species (5). The latter undergoes cycloaddition in the form (6) with the azomethine linkages of some heteroaromatic compounds (pyridine and quinoline) and of Schiff's bases.⁶ From benzaldehyde azine (3; Ar = Ph) and the diazenium salt (4; R = Ph) derived from *N*-methyl-*N*-nitrosoaniline and triethyloxonium tetrafluoroborate (Meerwein's reagent) we obtained a crystalline mono-cycloadduct (9; Ar = Ar' = Ph), identified on the basis of elemental analysis and spectra [τ -0.4 (s, H_a, collapsing on addition of D₂O), 0.85 (s, H_b), and 1.7-2.35 (complex m, 15 ArH), ν_{\max} 1 620, 1 610, and 1 575 (C:N) and 1 060 cm⁻¹ (BF₄⁻)]. No bis-adduct derived from cycloaddition with both azomethine linkages [*cf.* (3)] could be obtained, since protonation of the azine causes deactivation and the use of an auxiliary base had no effect (see Experimental section). The cycloaddition leads initially to the unisolable intermediate (8; Ar = Ar' = Ph) which spontaneously loses the elements of ethanol and a hydride ion [(8) \rightarrow (9)]. The dehydrogenating agent



has been shown to be the alkoxydiazonium salt itself,^{6b} an observation confirmed in our reaction. The cycloadducts with thiobenzoyl isocyanate⁷ and epoxides⁵ and the formation of the triazole (9) are the only reported cases in which one azomethine bond in an azine takes part in a cycloaddition. The triazolium salts we obtained from other azines are set out in Table 2. Electron donating groups (*p*-MeO, *m*- and *p*-Me) on the aryl

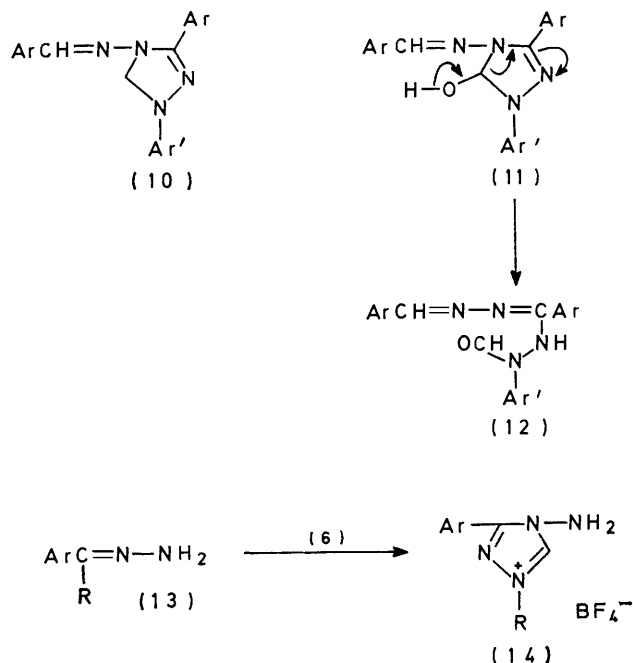
⁴ R. Huisgen, R. Grashey, E. Auferhaar, and R. Kunz, *Chem. Ber.*, 1965, **98**, 642.

⁵ M. Furukawa, M. Sugita, V. Kojima, and S. Hayashi, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**(9), 2088; 1974, **22**(7), 1468.

⁶ (a) T. Eicher, S. Hünig, and P. Nikolaus, *Angew. Chem. Internat. Edn.*, 1967, **6**, 699; *Chem. Ber.*, 1969, **102**, 3176; (b) T. Eicher, S. Hünig, H. Hansen, and P. Nikolaus, *ibid.*, p. 3159.

⁷ O. Tsuge and S. Kanemasa, *Bull. Chem. Soc. Japan*, 1972, **45**, 3591.

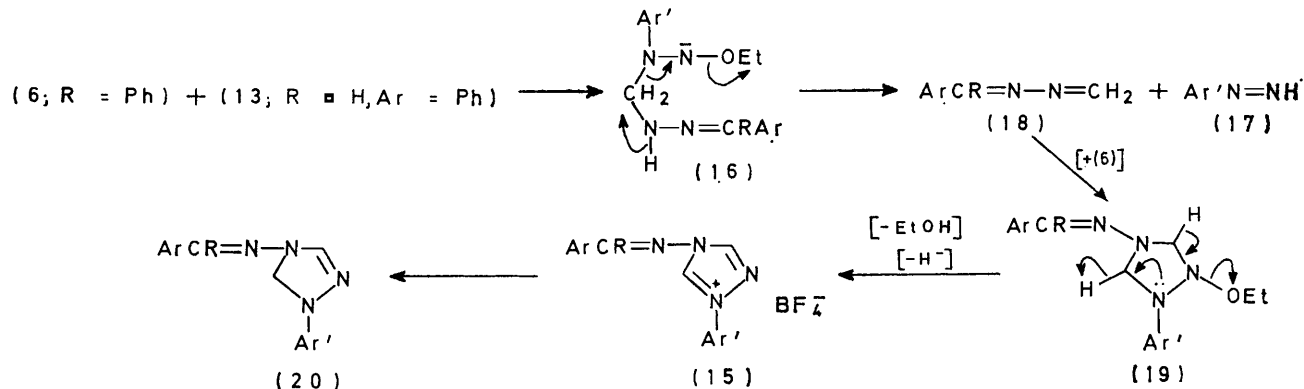
ring of the azine were found to speed up the reaction (from 72 to 24 h). This is probably due to increased basicity of the azine nitrogen facilitating conversion of the diazenium salt into the dipolar species [(4) \rightarrow (5)].



Surprisingly no reaction occurred between the salt (4; R = Ph) with an azine *ortho*-substituted with an

Ar = Ar' = Ph), a course of reaction which is noteworthy for such a mild nucleophile [also *cf.* (15) \rightarrow (20)], sodium carbonate cleaved the triazolium ring in (9; Ar = Ar' = Ph) to give the formylhydrazino-azine (12; Ar = Ar' = Ph) possibly by way of the carbinol-amine (11). The stability of the triazolium (10) in comparison with that of compound (9) may be due to the conjugated azomethine bond. Treatment of the fluoroborate (9) in cold dimethylformamide with aqueous hydrochloric acid precipitated the corresponding chloride (9; Cl for BF_4). Attempts to hydrolyse the exocyclic azomethine group in (9) or (10) to afford the corresponding *N*-aminotriazolium compound or *N*-aminotriazole gave tarry material and benzaldehyde.

It was thought that hydrazones (13; R = H) which possess both an azomethine and an amino-group might furnish the elusive *N*-aminotriazolium salts [(13) \rightarrow (14)] by cycloaddition with the dipole (6). A mild exothermic reaction ensued on mixing the hydrazone (13; R = H, Ar = Ph) with the reagent (4; R = Ph) in methylene chloride. The product showed no i.r. bands due to an amino-group but peaks at 1630, 1620, and 1580 cm^{-1} assigned to C=N stretching vibrations and a broad peak at 1060 cm^{-1} (BF_4^-). The n.m.r. spectrum ($\text{CF}_3\cdot\text{CO}_2\text{D}$) showed three one proton singlets (at τ -0.45, 0.35, and 0.65) and a ten-proton aromatic multiplet (τ 1.55–2.45). The singlet at -0.45 was removed on deuteration. These data were consistent with the structure (15; Ar = Ar' = Ph, R = H), which arises from a multi-step reaction as set out in the Scheme:



SCHEME

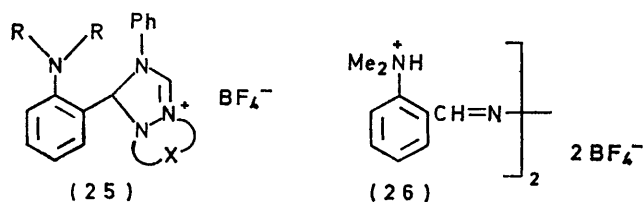
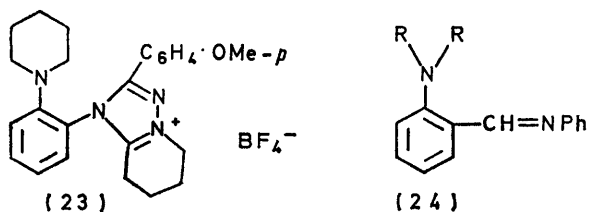
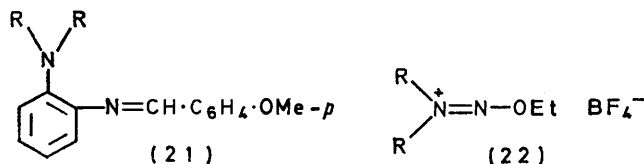
electron-releasing group, possibly owing to steric hindrance. Aromatic aldehyde azines with nitro-groups and aliphatic aldehyde azines as well as aliphatic and aromatic ketone azines also did not react, and the less reactive aliphatic alkoxydiazenium salts (22; RR = $[\text{CH}_2]_n$) gave only starting material with aromatic aldehyde azines. Benzaldehyde azines with *o*-dialkyl-amino-substituents (3; Ar = 2- $\text{R}_2\text{NC}_6\text{H}_4$) gave an immediate precipitate of the bistetrafluoroborate of the azine.

Some chemical reactions of the novel triazolium salts were explored. Reduction with sodium borohydride produced the triazolium (10; Ar = Ar' = Ph) from (9;

the 1,3-dipole (6; R = Ph) generated by proton abstraction from the methyl group in (4; R = Ph), by the hydrazone (13; R = H, Ar = Ph) interacts with (13; Ar = Ar' = Ph, R = H) to give (16; Ar = Ar' = Ph, R = H), which fragments to afford the aryldiazene (17; Ar' = Ph) and the unsymmetrical azine (18; Ar = Ph, R = H). The latter undergoes cycloaddition with the dipole (6; R = Ph) to yield in the usual way the triazolium salt (15; Ar = Ar' = Ph, R = H). The fate of the aryldiazene was not studied. The structure of (15) was also confirmed by reduction to the triazolium (20) with sodium borohydride. The mechanism and regio-specificity of this cycloaddition were supported by the

fact that the authentic azine (18; Ar = Ph, R = H) reacted with the diazenium salt (4; R = Ph) to give the triazolium salt (15; Ar = Ar' = Ph, R = H). The Scheme is analogous to the sequence put forward by Hünig⁶ for the reaction of aromatic amines with diazenium tetrafluoroborate which also leads to a triazolium salt, involving a diazo-compound and a Schiff's base as intermediates. Hydrazones derived from various aromatic aldehydes and ketones were used successfully (*cf.* Table 5). No reaction occurred when hydrazones of aliphatic ketones or aldehydes were employed.

The tendency of the azomethine bond in hetero-aromatic compounds such as pyridine, quinoline, and isoquinoline as well as in ordinary Schiff's bases such as benzylideneaniline to undergo cycloadditions with alkyldiazenium salts to form triazolium compounds has been widely explored.⁶ In view of the unusual effect an *ortho*-dialkylamino-group in arenes can exert ('t-amino'-effect)⁸ we treated the dialkylamino-substituted anil (21; RR = [CH₂]₅) with the diazenium salt (22; RR = [CH₂]₅) in dry methylene chloride. The



product was the triazolium compound (23) and the course of the reaction had thus not been influenced by the presence of the *o*-dialkylamino-group. The salt (23) was easily reduced to the corresponding triazoline with sodium borohydride. When the more reactive diazenium compound (4; R = Ph) was used the reaction gave only tarry material even at low temperature. The 'reverse' anil (24; RR = [CH₂]₅) in which the dialkylamino-group is on the potential aldehyde ring was also basic enough to convert the diazenium salts (22; RR = [CH₂]₆) into the corresponding 1,3-dipolar reagents by

proton abstraction, which led to the triazolium salts (25; X = [CH₂]₄ or [CH₂]₅), respectively, with no interference by the dialkylamino-group (for other examples see Experimental section).

The reactions of oximes and amidines which possess an azomethine unit (in the widest sense) either did not occur or gave tarry products.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 instrument, ¹H n.m.r. spectra with a Varian A60 or A100 instrument (Me₄Si as internal standard), and mass spectra with an A.E.I. MS12 instrument.

Preparation of Aromatic Aldehyde Azines.—The aldehyde (1 mol) was treated with hydrazine hydrate (0.5 mol) in ethanol on a boiling water-bath for 0.25 h. On cooling the azine crystallised out. New azines (recrystallised from ethanol) are set out in Table 1.

1,3-Diaryl-4-arylmethylene-1,2,4-triazolium Tetrafluoroborates (9).—In a typical preparation benzaldehyde azine (4.1 g) was added piecemeal to a stirred solution of 2-ethoxy-1-methyl-1-phenyldiazenium tetrafluoroborate⁹ (2.5 g) in dry dichloromethane (20 ml). The mixture was set aside for 76 h at room temperature, then poured into ether-water (2:1; 75 ml) and stirred for 3 h. (These were found to be the optimum conditions. The use of a tertiary base did not improve the yields.) The precipitated solid was filtered off, washed with ether, then water and recrystallised from aqueous ethanol to give white needles. Data are given in Tables 2 and 4. The reactions of aromatic aldehyde azines with 2-ethoxy-1,1-dialkyldiazenium tetrafluoroborates did not give identifiable products.

Reduction of Triazolium Tetrafluoroborates (9) with Sodium Borohydride.—4-Benzylideneamino-1,3-diphenyl-1,2,4-triazolium tetrafluoroborate (0.4 g) was reduced with sodium borohydride (0.02 g) in acetonitrile (20 ml) for 4 h at room temperature. The mixture was poured into water and the suspension extracted with chloroform (2 × 50 ml). The extract was dried (MgSO₄) and evaporated; chromatography of the resulting solid [Al₂O₃; light petroleum-ethyl acetate (2:1)] yielded the triazoline (10; Ar = Ar' = Ph) as needles (0.25 g, 78%), m.p. 123–125° (Found: C, 77.3; H, 5.5; N, 17.5. C₂₁H₁₈N₄ requires C, 77.3; H, 5.5; N, 17.1%). The 4-methoxy-isomer (10; Ar = *p*-MeO-C₆H₄, Ar' = Ph) produced by a similar procedure was obtained as yellow needles (50%), m.p. 135° (Found: C, 71.4; H, 5.7; N, 14.6. C₂₃H₂₂N₄O₂ requires: C, 71.7; H, 5.7; N, 14.5%).

Reaction of Triazolium Tetrafluoroborates (9) with Sodium Carbonate.—The 4-benzylideneamino-compound (9; Ar = Ar' = Ph) (5 g) was suspended in dichloromethane (50 ml) and water (50 ml). Anhydrous sodium carbonate (2 g) was added in portions and after stirring for 1 h the dichloromethane layer was separated, washed with water, dried (MgSO₄), and evaporated at 30 °C. The residue was chromatographed [Al₂O₃; light petroleum-ether (1:1)]. 1-(2-Formyl-2-phenylhydrazino)-1,4-diphenyl-2,3-diazabut-1,3-diene (12; Ar = Ar' = Ph) was obtained as needles (from cyclohexane) (2 g, 60%), m.p. 120° (Found: C, 73.8; H, 5.7; N, 16.7. C₂₁H₁₈N₄O requires C 73.7; H, 5.3; N, 16.3%). By a similar method the 4-methoxy-derivative (12; Ar = *p*-MeO-C₆H₄, Ar' = Ph) was obtained (42%);

⁸ O. Meth-Cohn and H. Suschitzky, *Adv. Heterocyclic Chem.*, 1972, 14, 211.

⁹ S. Hünig, G. Buttner, J. Cramer, L. Geldern, H. Hansen, and E. Lucke, *Chem. Ber.*, 1969, 102, 2093.

TABLE 1
 2-Dialkylaminobenzaldehyde azines (3)

2-Amino-group	Yield (%)	M.p. (°C)	Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
Me ₂ NH	80	150	73.4	7.7	18.5	C ₁₈ H ₂₂ N ₄	73.5	7.5	19.0
C ₆ H ₅ N-	70	140	76.0	7.0	16.5	C ₂₂ H ₂₆ N ₄	76.3	7.5	16.2
C ₆ H ₁₀ N-	75	160	76.8	8.3	14.6	C ₂₄ H ₃₀ N ₄	77.0	8.0	14.9
Morpholino	60	212	69.8	6.7	14.8	C ₁₂ H ₂₆ N ₄ O	69.9	6.9	14.8

TABLE 2

1,3-Diaryl-4-arylmethyleneamino-1,2,4-triazolium tetrafluoroborates (9) from azines and alkoxydiazonium salts

Compound (9)		M.p. (°C)	Yield (%)	Reaction time (h)	Found (%)			Formula	Required (%)		
Ar	Ar'				C	H	N		C	H	N
Ph	Ph	225	36	76	61.0	4.3	13.7	C ₂₁ H ₁₇ BF ₄ N ₄	61.2	4.1	13.6
Ph	<i>p</i> -MeC ₆ H ₄	268	23	24	61.9	4.2	12.7	C ₂₃ H ₁₉ BF ₄ N ₄	62.0	4.5	13.1
<i>p</i> -MeC ₆ H ₄	Ph	230	40	24	62.5	4.8	12.7	C ₂₃ H ₂₁ BF ₄ N ₄	62.7	4.8	12.7
<i>p</i> -MeO-C ₆ H ₄	Ph	237	36	24	58.0	4.2	11.7	C ₂₃ H ₂₁ BF ₄ N ₄ O ₂	58.5	4.4	11.8
<i>m</i> -MeO-C ₆ H ₄	Ph	180	21	24	58.7	4.6	12.0	C ₂₃ H ₂₁ BF ₄ N ₄ O ₂	58.5	4.4	11.8
2-Furyl	Ph	242	51	24	52.0	3.2	14.2	C ₁₇ H ₁₃ BF ₄ N ₄ S ₂	52.0	3.3	13.2
1-Naphthyl	Ph	240	6	24	68.0	4.4	10.8	C ₂₆ H ₂₁ BF ₄ N ₄	68.0	4.1	10.9
2-Thienyl	Ph	218	50	5	47.9	3.5	12.9	C ₁₇ H ₁₃ BF ₄ N ₄ S ₂	48.1	3.0	13.2

TABLE 3

Bistetrafluoroborates of *o*-dialkylaminebenzaldehyde azines (26)

<i>o</i> -Substituent	M.p. (°C)	Yield (%)	Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
Me ₂ N	270	75	45.7	4.9	11.5	C ₁₈ H ₂₄ B ₂ F ₈ N ₄	46.0	5.1	11.9
C ₆ H ₅ N	196	80	50.5	5.1	10.5	C ₂₂ H ₂₆ B ₂ F ₈ N ₄	50.7	5.4	10.7
C ₆ H ₁₀ N	230	70	52.2	5.7	10.1	C ₂₄ H ₃₂ B ₂ F ₈ N ₄	52.4	5.8	10.1

m.p. 140° (Found: C, 68.3; H, 5.7; N, 13.8. C₂₃H₂₂N₄O₃ requires C, 68.7; H, 5.5; N, 13.9%).

Conversion of Triazolium Tetrafluoroborates (9) into Chlorides.—The salt (9; Ar = 2-thienyl, Ar' = Ph) (1 g) was dissolved in dimethylformamide (7 ml) and hydrochloric acid (20%) was added until precipitation ceased. Recrystallisation from ethanol gave the *chloride* (9; Ar = 2-thienyl, Ar' = Ph, Cl for BF₄) (75%), m.p. 260° (Found: C, 54.4; H, 3.2; N, 14.6. C₁₇H₁₃ClN₄S₂ requires C, 54.8; H, 3.5; N, 15.0%). By a similar method the *salt* (9; Ar = Ar' = Ph, Cl for BF₄) was obtained (87%); m.p. 280° (Found: C, 71.2; H, 4.5; N, 15.6. C₂₁H₁₇ClN₄ requires C, 70.0; H, 4.7; N, 15.5%).

Reactions of o-Dialkylaminobenzaldehyde Azines with the Diazonium Tetrafluoroborate (4; R = Ph).—The *o*-dialkylaminobenzaldehyde azine (0.1 mol), when added to a solution of 2-ethoxy-1-methyl-1-phenyldiazonium tetrafluoroborate (0.1 mol) in methylene chloride, gave an immediate precipitate of the azine salt, which was filtered off and washed with ether. The bis-salts thus obtained are set out in Table 3.

1-Aryl-4-arylmethyleneamino-1,2,4-triazolium Tetrafluoroborates (15).—The hydrazone (0.1 mol) prepared by a conventional method was added in portions with stirring to a solution of the diazenium salt (4; R = Ph or *p*-MeC₆H₄) in dry dichloromethane (20 ml) at room temperature. The mixture was stirred for 5 h and then poured into ether-water (2:1; 75 ml). The precipitate was washed with water and recrystallised from water to give the title compound. The results are listed in Tables 5 and 6.

Benzaldehyde hydrazone¹⁰ and the diazenium tetrafluoroborate (4; R = Ph) gave, by the above procedure, 4-

benzylideneamino-1-phenyl-1,2,4-triazolium tetrafluoroborates (15; Ar = Ar' = Ph, R = H) (30%).

Acidic Hydrolysis of Triazolium Tetrafluoroborates (9).—On heating the benzylideneamino-compound (9; Ar = Ar' = Ph) in aqueous hydrochloric acid (20%) for 3 h only

TABLE 4

¹H N.m.r. data for the triazolium tetrafluoroborates (9)

Ar	Ar'	τ(CF ₃ ·CO ₂ D)
Ph	Ph	−0.4 (1 H, s), * 0.85 (1 H, s), 1.7—2.35 (15 H, m)
Ph	<i>p</i> -MeC ₆ H ₄	−0.25 (1 H, s), * 0.9 (1 H, s), 1.65—2.6 (14 H, m), 7.6 (s, Me)
<i>p</i> -MeC ₆ H ₄	Ph	−0.25 (1 H, s), * 0.95 (1 H, s), 1.7—2.65 (13 H, m), 7.55 (2 s, Me)
<i>p</i> -MeO-C ₆ H ₄	Ph	−0.25 (1 H, s), * 0.95 (1 H, s), 1.8—2.6 (13 H, m), 6.00 (s, 2 OMe)
<i>m</i> -MeO-C ₆ H ₄	Ph	−0.45 (1 H, s), * 0.7 (1 H, s), 1.8—2.6 (13 H, m), 5.9 (s, 2 OMe)
2-Furyl	Ph	−0.3 (1 H, s), * 1.0 (1 H, s), 1.8—3.0 (11 H, m)
2-Thienyl	Ph	−0.3 (1 H, s), * 0.7 (1 H, s), 1.6—2.8 (11 H, m)
2-Naphthyl	Ph	−0.3 (1 H, s), * 0.4 (1 H, s), 1.7—2.5 (19 H, m)

* Removed on addition of D₂O.

benzaldehyde (apart from tarry material) was obtained. Other compounds of this group behaved similarly.

Reduction of Triazolium Tetrafluoroborates.—The benzylideneamino-compound (15; Ar = Ar', R = H), (0.3 g) was reduced with sodium borohydride (0.05 g) in acetonitrile (10 ml) for 2 h with stirring. On pouring the mixture into water a precipitate was obtained which on recrystallisation from light petroleum gave the *triazolime* (20; Ar =

¹⁰ H. J. Bestmann and H. Fritzsche, *Chem. Ber.*, 1961, **94**, 2477.

Ar' = Ph, R = H) as yellow needles (0.19 g, 50%), m.p. 70° (Found: C, 71.8; H, 5.3; N, 22.2. C₁₅H₁₄N₄ requires C, 72.0; H, 5.6; N, 22.4%). 4-(2-Chlorobenzylideneamino)-1-phenyl-1,2,4-triazolium tetrafluoroborate was reduced by a similar method to the corresponding *triazoline* (75%), m.p. 138–40° (from ethanol) (Found: C, 63.7;

1-ethoxyiminopiperidinium tetrafluoroborate (22; RR = [CH₂]₅) (2.3 g) in dry methylene chloride in the usual way to give the *triazolium salt* (23) (2.3 g, 50%), m.p. 170° (Found: C, 60.9; H, 6.6; N, 12.0. C₂₄H₂₉BF₄N₄ requires C, 60.5; H, 6.1; N, 11.7%), τ (CF₃CO₂D) 8.5 and 8.0 (m, 6 H and 4 H, respectively), 6.9 (2 H, m), 6.15 (s, OMe),

TABLE 5
1-Aryl-4-arylmethyleneamino-1,2,4-triazolium tetrafluoroborates (15)

Ar	H	Ar'	M.p. (°C)	Yield (%)	Reaction time (h)	Found (%)			Formula	Required (%)		
						C	H	N		C	H	N
Ph	H	Ph	125	20	5	53.2	3.8	16.3	C ₁₅ H ₁₃ BF ₄ N ₄	53.6	3.9	16.6
<i>p</i> -MeC ₆ H ₄	H	Ph	157	42	20	55.1	4.2	16.0	C ₁₆ H ₁₅ BF ₄ N ₄	54.9	4.3	16.0
<i>o</i> -MeO·C ₆ H ₄	H	Ph	140	27	4	52.4	4.3	15.1	C ₁₆ H ₁₅ BF ₄ N ₄	52.5	4.1	15.3
<i>m</i> -NO ₂ ·C ₆ H ₄	H	Ph	224	46	20	47.4	3.1	18.1	C ₁₅ H ₁₂ BF ₄ N ₅ O ₂	47.2	3.1	18.3
<i>o</i> -ClC ₆ H ₄	H	Ph	170	27	20	49.1	3.1	15.5	C ₁₅ H ₁₂ BClF ₄ N ₄	48.6	3.2	15.1
Ph	Me	Ph	178	28	4	54.7	4.1	15.5	C ₁₆ H ₁₅ BF ₄ N ₄	54.9	4.3	16.0
Ph	Ph	Ph	202	37	4	61.0	4.0	13.2	C ₂₁ H ₁₇ BF ₄ N ₄	61.2	4.1	13.6
Ph	Me	<i>p</i> -MeC ₆ H ₄	208	27	20	56.1	4.2	15.3	C ₁₇ H ₁₇ BF ₄ N ₄	56.0	4.7	15.3
Ph	H	<i>p</i> -MeC ₆ H ₄	200	58	10	55.1	4.1	16.1	C ₁₆ H ₁₅ BF ₄ N ₄	54.9	4.3	16.0

TABLE 6

¹H N.m.r. data for 1-aryl-4-arylmethyleneamino-1,2,4-triazolium tetrafluoroborates (15)

Ar	R	Ar'	Solvent	τ
Ph	H	Ph	CF ₃ ·CO ₂ D	-0.45 (1 H, s), * 0.35 (1 H, s), 0.65 (1 H, s), 1.55–2.45 (10 H, m)
<i>p</i> -MeC ₆ H ₄	H	Ph	(CD ₃) ₂ SO	-1.7 (1 H, s), * 0.2 (1 H, s), 0.6 (1 H, s), 1.7–2.7 (9 H, m), 7.5 (s, Me)
<i>o</i> -MeO·C ₆ H ₄	H	Ph	(CD ₃) ₂ SO	-1.7 (1 H, s), * -0.2 (1 H, s), 0.35 (1 H, s), 1.65–2.85 (9 H, m), 5.95 (s, OMe)
<i>m</i> -NO ₂ ·C ₆ H ₄	H	Ph	CF ₃ ·CO ₂ D	-0.45 (1 H, s), * 0.55 (1 H, s), 0.6 (1 H, s), 1.1–2.3 (9 H, m)
<i>o</i> -ClC ₆ H ₄	H	Ph	(CD ₃) ₂ SO	-1.8 (1 H, s), * -0.3 (1 H, s), 0.27 (1 H, s), 1.5–2.5 (9 H, m)
Ph	Me	Ph	CF ₃ ·CO ₂ D	0.05 (1 H, s), * 1.5 (1 H, s), 1.5–2.7 (10 H, m), 7.3 (s, Me)
Ph	Ph	Ph	(CD ₃) ₂ SO	-1.45 (1 H, s), * 0.75 (1 H, s), 2.2–5 (15 H, m)
Ph	Me	<i>p</i> -MeC ₆ H ₄	CF ₃ ·CO ₂ D	0.0 (1 H, s), * 1.05 (1 H, s), 1.8–2.55 (9 H, m), 7.35 (s, Me), 7.55 (s, Me)
Ph	H	<i>p</i> -MeC ₆ H ₄	CF ₃ ·CO ₂ D	-0.2 (s, 1 H), * 0.85 (1 H, s), 0.9 (1 H, s), 1.8–2.5 (9 H, m), 7.6 (s, Me)

* Removed on addition of D₂O.

TABLE 7

3-(*o*-Dialkylaminophenyl)-4-phenyl-1,2,4-triazolium tetrafluoroborates (25)

R	X	Yield (%)	M.p. (°C)	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
Me	[CH ₂] ₄	30	170	59.3	5.6	13.5	C ₂₀ H ₂₃ BF ₄ N ₄	59.1	5.7	13.8
Me	[CH ₂] ₅	25	192	59.7	5.8	12.9	C ₂₁ H ₂₅ BF ₄ N ₄	60.0	6.0	13.3
[CH ₂] ₅	[CH ₂] ₄	35	185	62.2	6.5	12.4	C ₂₃ H ₂₇ BF ₄ N ₄	61.9	6.1	12.5
[CH ₂] ₅	[CH ₂] ₅	40	240	62.5	6.7	12.6	C ₂₄ H ₂₉ BF ₄ N ₄	62.6	6.3	12.1
[CH ₂] ₂ ·O·[CH ₂] ₂	[CH ₂] ₄	20	200	60.2	5.7	12.5	C ₂₂ H ₂₅ BF ₄ N ₄ O	58.9	5.6	12.5

H, 4.8; N, 19.8. C₁₅H₁₃ClN₄ requires C, 63.4, H, 4.6; N, 9.7%).

3-(2-Dialkylaminophenyl)-4-phenyl-1,2,4-triazolium Tetrafluoroborates (25).—The 2-dialkylaminobenzylideneaniline ¹¹ (24; RR = Me₂, [CH₂]₅, or [CH₂]₂·O·[CH₂]₂) (0.1 g) was added in portions to a solution of the appropriate alkoxy-diazonium salt (0.1 g) in dry dichloromethane at 0 °C and the mixture was stirred for 7 h. The triazolium salt which separated was filtered off, washed with cold water, and recrystallised from ethanol. Results are set out in Table 7.

5,6,7,8-Tetrahydro-2-(4-methoxyphenyl)-1-(2-piperidinophenyl)-1H-pyrido[1,2-b][1,2,4]triazolium Tetrafluoroborate (23).—The anil (21; RR = [CH₂]₅) (3 g) was treated with

5.95 (2 H, m), and 2–3.15 (8 H, m). On reduction with sodium borohydride in acetonitrile for 3 h and work-up as previously described, 1,5,6,7,8,8a-hexahydro-2-(4-methoxyphenyl)-1-(2-piperidinophenyl)pyrido[1,2-b][1,2,4]triazole (64%), m.p. 100°, was obtained (Found: C, 73.5; H, 7.2; N, 14.2. C₂₄H₃₀N₄O requires C, 73.9; H, 7.7; N, 14.3%).

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¹¹ R. L. Bentley, Ph.D. Thesis, University of Salford, 1974.