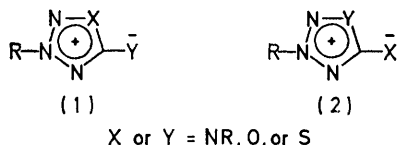


## Cyclic Meso-ionic Compounds. Part 17.<sup>1</sup> Synthesis, Spectroscopic Properties, and Chemistry of 1,2,3,4-Oxatriazolium-5-aminides and 1,2,3,4-Tetrazolium-5-olates

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Derivatives of the isomeric meso-ionic 1,2,3,4-oxatriazolium-5-aminides (3) and 1,2,3,4-tetrazolium-5-olates (4) have been prepared and characterised and their interconversion (3  $\rightleftharpoons$  4) has been examined. 3-Phenyl-1,2,3,4-oxatriazolium-5-anilide (3a) undergoes a 1,3-dipolar cycloaddition with *p*-chlorophenyl isocyanate. The 1,2,3,4-tetrazolium-5-olates (4) form tetrafluoroborate salts when treated with triethyloxonium tetrafluoroborate.

IN continuation of our studies on pairs of meso-ionic isomers of the general types (1) and (2), we have now explored the synthesis and characterisation of derivatives of the meso-ionic 1,2,3,4-oxatriazolium-5-aminides (3) and 1,2,3,4-tetrazolium-5-olates (4).



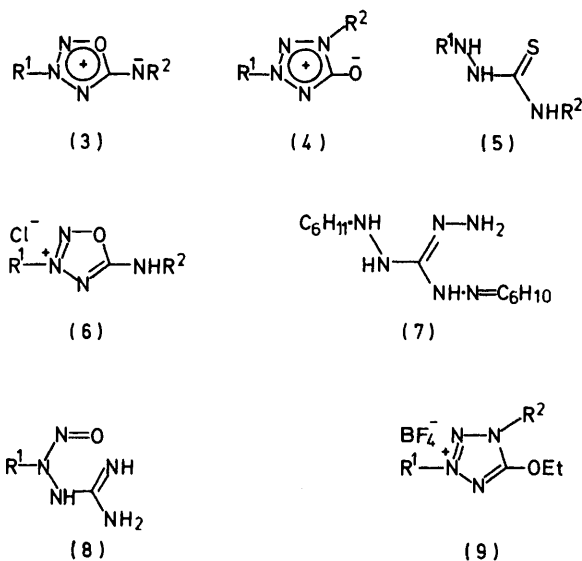
The oxatriazoliumaminides (3) were first encountered by Busch and Becker,<sup>2</sup> who treated 1,4-diphenylthiosemicarbazide (5a) with nitrous acid and obtained the chloride (6a) which with base gave the oxatriazolium-anilide (3a). Later, several more derivatives of (3) were obtained by Busch and Schmidt.<sup>3</sup> In these two early investigations,<sup>2,3</sup> their meso-ionic structure (3) was not recognised, but recently Christopherson and Treppendahl<sup>4</sup> have prepared a number of the chlorides (6; R<sup>2</sup> = H) from 1-substituted and 1,4-disubstituted thiosemicarbazides (5) and nitrous acid. Originally, the heterocycles (3) had been assigned bicyclic structures,<sup>2,3</sup> but Christopherson and Treppendahl<sup>4</sup> have reformulated them as meso-ionic 1,2,3,4-oxatriazolium-5-aminides (3), a proposal which is in full agreement with our results.

Other routes now recognised as leading to the meso-ionic compounds (3) have been described. Treatment of compound (8) with nitrous acid gave the oxatriazoliumaminide (3; R<sup>1</sup> = C<sub>6</sub>H<sub>11</sub>, R<sup>2</sup> = N=C<sub>6</sub>H<sub>10</sub>), presumably by azide elimination.<sup>5</sup> The nitroso-compound (8; R<sup>1</sup> = C<sub>6</sub>H<sub>11</sub>) with hot dilute hydrochloric acid or concentrated hydrochloric acid at room temperature gave the oxatriazolium chloride (6; R<sup>1</sup> = C<sub>6</sub>H<sub>11</sub>, R<sup>2</sup> = H).<sup>5</sup> The chlorides (6; R<sup>2</sup> = H) have also been prepared by treatment of *N*-aryl-*N'*-cyano-*N*-nitrosohydrazines [RN(NO)NH·CN], prepared from *N*-aryl-*N'*-cyanohydrazines (RNH·NH·CN) and nitrous acid, with hydrogen chloride.<sup>6</sup> Treatment of the chloride (6; R<sup>1</sup> = Ph, R<sup>2</sup> = H) with aqueous sodium hydrogen carbonate is reported to yield the yellow, crystalline meso-ionic oxatriazoliumaminide (3; R<sup>1</sup> = Ph, R<sup>2</sup> = H).<sup>6</sup>

We have prepared the chlorides (6a—e) by treatment

of ethanolic solutions of 1,4-diarylthiosemicarbazides (5a—e) with pentyl nitrite and hydrogen chloride. Without characterisation, the yellow, crystalline chlorides (6a—e) were suspended in chloroform and treatment with dry ammonia gave the deep red oxatriazoliumaminides (3a—e).

The spectroscopic properties of compounds (3a—e) support their formulation as meso-ionic compounds. Their i.r. spectra show a strong absorption in the C=N stretching region (1 675—1 680 cm<sup>-1</sup>) and the n.m.r. spectra are in accord with the proposed structures. Their u.v. and visible spectra are exemplified by those of (3a) [ $\lambda_{\text{max}}$ . 265 and 410 nm ( $\epsilon$  31 120 and 2 539)]. The mass spectra all show a molecular ion and fragmentation



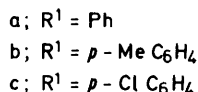
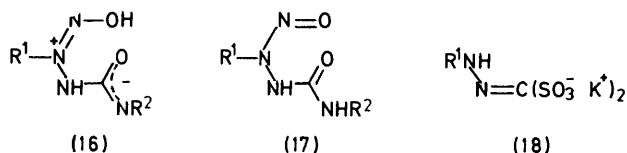
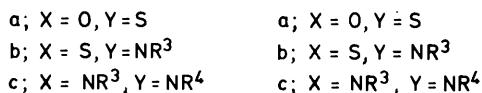
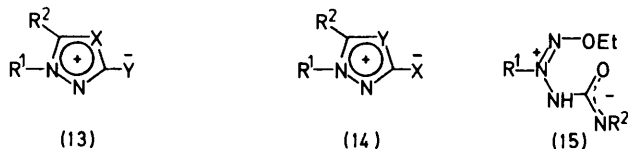
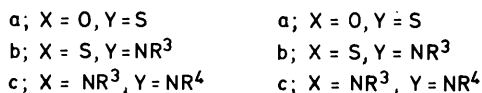
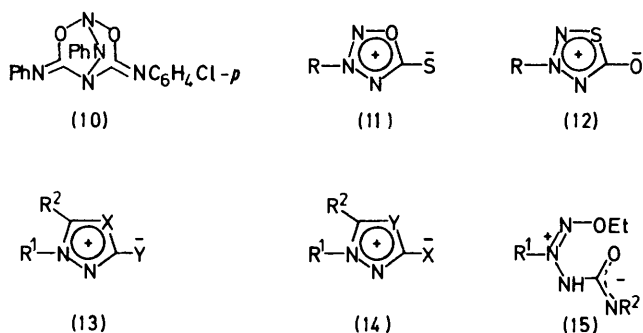
- a; R<sup>1</sup> = R<sup>2</sup> = Ph  
 b; R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>  
 c; R<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Ph  
 d; R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 e; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Ph  
 f; R<sup>1</sup> = R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>  
 g; R<sup>1</sup> = R<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>

patterns consistent with the structures (3a—e); a detailed analysis of the mass spectra of meso-ionic heterocycles of the general types (1) and (2) is given in Part 20.<sup>7</sup> Dipole moments of the compounds (3a, d, and e) in benzene solution have been reported elsewhere,<sup>8</sup>

and the results strongly support the meso-ionic structure (3); the dipole moment of (3a) was found to be 5.4 D.

Compounds (3a—e) are all deep red and crystalline. Treatment with hydrogen chloride regenerates the chlorides (6). When the 3-phenyl compound (3a) and *p*-chlorophenyl isocyanate in toluene were heated under reflux (72 h), the 3-phenyl-5-*p*-chloroanilide (3d) and starting material (3a) (3 : 1) were isolated. The most reasonable mechanism for the formation of (3d) is by 1,3-dipolar cycloaddition of *p*-chlorophenyl isocyanate to (3a) giving the bicyclic adduct (10) which may then lose phenyl isocyanate in a reverse 1,3-dipolar cycloaddition giving the product (3d). This is the first example of a meso-ionic heterocycle of the general type (1) participating in a 1,3-dipolar cycloaddition.

Busch and Schmidt<sup>3</sup> found that treatment of compounds (3) with aqueous ethanolic alkali resulted in a rearrangement which can now be interpreted in terms of an isomerisation yielding the meso-ionic 1,2,3,4-tetrazolium-5-olates (4). This transformation is analogous to the rearrangement of the meso-ionic oxatriazoliumthiolates (11) to the thiatrizoliumolates (12) in ethanolic ammonia,<sup>1,9</sup> and to the rearrangement (13a—c) → (14a—c) in pure ethanol which we have previously



described.<sup>10-12</sup> By employing this rearrangement (3 → 4), we have prepared the derivatives (4a—e) of the meso-ionic tetrazoliumolates (4). In previous studies,<sup>10-12</sup> we have suggested that the rearrangements (11) → (12) and (13a—c) → (14a—c) may proceed *via* a betaine intermediate. In a similar manner, the rearrangements (3a—e) → (4a—e) may well involve

betaines of the type (15), but we cannot exclude the possibility that a betaine (16) or its tautomer (17) is an intermediate.

Representatives of the meso-ionic tetrazoliumolates (4) were in fact first encountered by von Pechmann, who treated potassium phenylhydrazonomethanedisulphonate [PhNH·N=C(SO<sub>3</sub><sup>-</sup>K<sup>+</sup>)<sub>2</sub>] with benzenediazonium

salts.<sup>13</sup> A similar synthesis involving the reaction of benzenediazonium salts with bis(ethylsulphonyl)methane [CH<sub>2</sub>(SO<sub>2</sub>Et)<sub>2</sub>]<sup>14,15</sup> or with dinitromethane [CH<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>15</sup> has been reported to yield the tetrazoliumolates (4). In order to make a direct comparison of compounds (4), prepared by the rearrangement of oxatriazoliumaminides (3), with samples prepared by an alternative route, we have synthesised several derivatives using the method of von Pechmann.<sup>13</sup>

The disulphonates (18) [ArNH·N=C(SO<sub>3</sub><sup>-</sup>K<sup>+</sup>)<sub>2</sub>] were prepared from arenediazonium acetates and potassium diazomethanedisulphonate-potassium sulphite addition product in aqueous solution. Treatment of the disulphonates (18) with diazonium salts afforded the tetrazoliumolates (4a, f, and g) (Scheme 1). Compound (4a) was identical with a sample prepared by rearrangement of compound (3a). We have found that this route is only suitable for the synthesis of compounds (4) in which the aryl substituents are identical (4; R<sup>1</sup> = R<sup>2</sup>). Attempts to prepare the derivatives (4; R<sup>1</sup> ≠ R<sup>2</sup>) resulted in a mixture (*ca.* 1 : 1) of the desired product (4; R<sup>1</sup> = R<sup>2</sup>) and the symmetrically substituted product (4; R<sup>1</sup> ≠ R<sup>2</sup>). The latter compounds probably arise by a diazonium exchange reaction of the disulphonates (18) (Scheme 2). The approximate composition of the mixtures was determined by mass spectrometry.

The colourless, crystalline meso-ionic tetrazoliumolates (4a—g) are quite distinct from the red, crystalline meso-ionic oxatriazoliumaminides (3a—e). The i.r. spectra of (4a—g) show a strong absorption in the region 1 695—1 700 cm<sup>-1</sup> which is characteristic of the C=O stretching vibration. Their u.v. and visible spectra are consistent with the meso-ionic structure (4); the spectrum of (4a) is typical [ $\lambda_{\text{max}}$  225, 263, and 326 nm ( $\epsilon$  35 110, 25 280, and 32 430)]. The n.m.r. spectra account for the aryl substituents and the mass spectra

all show a molecular ion. Dipole moments of the tetrazoliumolates (4a, d, and e) have been reported.<sup>8</sup> The results strongly support the meso-ionic structure (4); the dipole moment of (4a) in benzene solution was found to be 5.4 D.

The tetrazoliumolates (4) appear to be unreactive towards 1,3-dipolarophiles. Treatment with triethyl-oxonium tetrafluoroborate gives the colourless, crystalline tetrafluoroborates (9a, d—g) in high yield.

#### EXPERIMENTAL

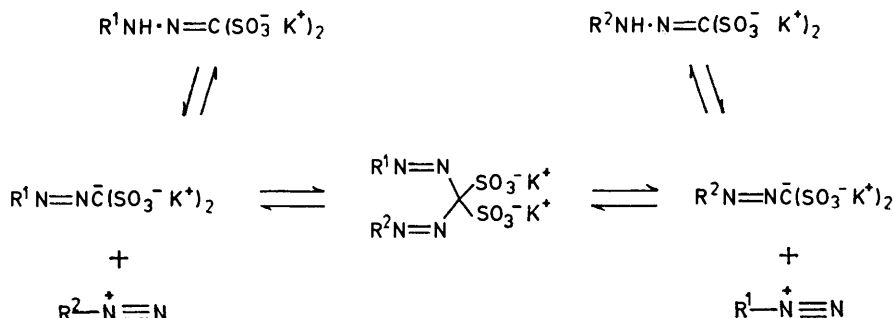
General experimental details are given in Part 8.<sup>16</sup>

**3-Aryl-1,2,3,4-oxatriazolium-5-amidines (3).**—Pentyl nitrite (5.9 g) was added to a suspension of 1,4-diphenylthiosemicarbazide (5a) (2.4 g) in ethanol (100 ml) and the mixture cooled to 0°. After saturation with hydrogen chloride, the solution was filtered and concentrated. Addition of ether to the filtrate and cooling gave a yellow, crystalline precipitate of 5-anilino-3-phenyl-1,2,3,4-oxatriazolium chloride (6a) which was washed with ether and suspended in dry chloroform (100 ml). Dry ammonia was passed through the suspension yielding a deep red solution

(2.3 g, 84%), carmine needles, m.p. 153° [Found: C, 57.0; H, 3.5; N, 20.8;  $M^+$ , 272 (<sup>35</sup>Cl)].  $C_{13}H_9ClN_4O$  requires C, 57.2; H, 3.3; N, 20.6%;  $M$ , 272 (<sup>35</sup>Cl)];  $\lambda_{max}$ , 270 and 416 nm ( $\epsilon$  28 750 and 2 410);  $\nu_{max}$ , 1 680  $cm^{-1}$ ;  $\tau$  1.93 and 2.41 ( $A_2B_2$ ,  $J_{AB}$  9 Hz,  $p-ClC_6H_4$ ) and 2.67 (s, Ph).

**Reaction of 3-Phenyl-1,2,3,4-oxatriazolium-5-anilide (3a) with *p*-Chlorophenyl Isocyanate.**—Compound (3a) (0.2 g) and *p*-chlorophenyl isocyanate (0.3 g) (freshly distilled) in toluene (10 ml) were heated under reflux (72 h). The mixture was poured into cold water (50 ml) and set aside (24 h). Evaporation and extraction with benzene gave a red solution. The residue (0.1 g) was identified as a mixture of diphenylurea and di-*p*-chlorophenylurea. Evaporation of the benzene solution gave a dark mixture (0.2 g) which was separated by t.l.c. (silica gel; chloroform). Two red bands were collected. The first band ( $R_F$  ca. 0.55) afforded a red solid which was identified as 3-phenyl-1,2,3,4-oxatriazolium-5-*p*-chloroanilide (3d) (0.12 g, 55%), m.p. 129°, identical with an authentic sample. The second band ( $R_F$  ca. 0.45) gave a red solid which was identified as starting material (3a) (0.04 g).

**Potassium Arylhydrazonomethanedisulphonates (18).**—An aqueous solution of benzenediazonium chloride, prepared



SCHEME 2

which on filtration and evaporation gave a crystalline residue. Recrystallisation from light petroleum (b.p. 60—80°) gave 3-phenyl-1,2,3,4-oxatriazolium-5-anilide (3a) (0.9 g, 39%) as dark red needles, m.p. 110—111° (lit.,<sup>2</sup> 110°) (Found: C, 65.55; H, 4.0; N, 23.5%;  $M^+$ , 238. Calc. for  $C_{13}H_{10}N_4O$ : C, 65.5; H, 4.2; N, 23.5%;  $M$ , 238);  $\lambda_{max}$ , 265 and 410 nm ( $\epsilon$  31 120 and 2 539);  $\nu_{max}$ , 1 680  $cm^{-1}$ ;  $\tau$  1.8—3.0 (m, ArH).

The following compounds were similarly prepared: 3-phenyl-1,2,3,4-oxatriazolium-5-*p*-toluidide (3b) (0.8 g, 33%), lustrous red plates, m.p. 123° (Found: C, 66.4; H, 4.8; N, 22.5%;  $M^+$ , 252.  $C_{14}H_{12}N_4O$  requires C, 66.7; H, 4.8; N, 22.2%;  $M$ , 252);  $\lambda_{max}$ , 267 and 422 nm ( $\epsilon$  43 000 and 2 350);  $\nu_{max}$ , 1 680  $cm^{-1}$ ;  $\tau$  1.8—3.0 (m, 9 ArH) and 7.68 (s, Me); 3-*p*-tolyl-1,2,3,4-oxatriazolium-5-anilide (3c) (0.9 g, 37%), crimson plates, m.p. 128° (lit.,<sup>3</sup> 127°) (Found: C, 66.5; H, 5.0; N, 22.0%;  $M^+$ , 252. Calc. for  $C_{14}H_{12}N_4O$ : C, 66.7; H, 4.8; N, 22.2%;  $M$ , 252);  $\lambda_{max}$ , 235 inf., 270, and 406 nm ( $\epsilon$  9 550, 20 410, and 3 638);  $\nu_{max}$ , 1 685  $cm^{-1}$ ;  $\tau$  1.96 and 2.58 ( $A_2B_2$ ,  $J_{AB}$  8 Hz,  $p-MeC_6H_4$ ), 2.63 (s, Ph), and 7.52 (s, Me); 3-phenyl-1,2,3,4-oxatriazolium-5-*p*-chloroanilide (3d) (1.2 g, 44%), maroon plates, m.p. 129° [Found: C, 57.2; H, 3.6; N, 20.6%;  $M^+$ , 272 (<sup>35</sup>Cl)].  $C_{13}H_9ClN_4O$  requires C, 57.2; H, 3.3; N, 20.6%;  $M$ , 272 (<sup>35</sup>Cl)];  $\lambda_{max}$ , 269 and 402 nm ( $\epsilon$  43 550 and 3 338);  $\nu_{max}$ , 1 680  $cm^{-1}$ ;  $\tau$  1.8—2.4 (m,  $p-ClC_6H_4$ ) and 2.70 (s, Ph); 3-*p*-chlorophenyl-1,2,3,4-oxatriazolium-5-anilide (3e)

from aniline (27.0 g), was treated with a saturated solution of lead acetate. The precipitated lead chloride was collected and the diazonium acetate solution was slowly added with stirring to a slurry of potassium diazomethanedisulphonate—potassium sulphite addition product (93.0 g) and water (250 ml). After standing overnight, the solution was filtered and concentrated. Addition of ethanol gave potassium phenylhydrazonomethanedisulphonate (18a) (70.0 g, 97%) as a powder,  $\tau(D_2O)$  2.5—2.9 (m, ArH), which was used without further purification.

The following derivatives were similarly prepared: potassium *p*-tolylhydrazonomethanedisulphonate (18b) (76.6 g, 97%), white powder,  $\tau(D_2O)$  2.77 (s, 4 ArH) and 7.70 (s, Me); potassium *p*-chlorophenylhydrazonomethanedisulphonate (18c) (78.0 g, 94%), yellow powder,  $\tau$  2.5—2.7 (m, ArH).

**1,3-Diaryl-1,2,3,4-tetrazolium-5-olates (4).**—(a) *From 3-aryl-1,2,3,4-oxatriazolium-5-aminides (3).* Compound (3a) (1.0 g) was dissolved in ethanol (30 ml) and 10M-sodium hydroxide solution (5 ml) was added. The mixture was heated to its boiling point when the deep red colour was discharged. When the resulting pale yellow solution was cooled and diluted with water, a crystalline precipitate formed. After washing with water and drying, this product was recrystallised from carbon tetrachloride giving 1,3-diphenyl-1,2,3,4-tetrazolium-5-olate (4a) (0.9 g, 90%), m.p. 157° (lit.,<sup>13</sup> 157°) (Found: C, 65.2; H, 4.1; N, 23.3%;

$M^+$ , 238. Calc. for  $C_{13}H_{10}N_4O$ : C, 65.5; H, 4.2; N, 23.5%;  $M$ , 238;  $\lambda_{\max}$ , 225, 263, and 326 nm ( $\epsilon$  35 100, 25 280, and 32 430);  $\nu_{\max}$ , 1 695  $cm^{-1}$ ;  $\tau$  1.7—2.5 (m, ArH).

The following compounds were similarly prepared: 3-phenyl-1-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4b) (0.8 g, 80%), needles, m.p. 200° (Found: C, 66.6; H, 4.8; N, 22.5%;  $M^+$ , 252.  $C_{14}H_{12}N_4O$  requires C, 66.7; H, 4.8; N, 22.2%;  $M$ , 252);  $\lambda_{\max}$ , 225, 261, and 330 nm ( $\epsilon$  36 850, 24 880, and 34 650);  $\nu_{\max}$ , 1 695  $cm^{-1}$ ;  $\tau$  1.8—2.6 (m, 9 ArH) and 7.58 (s, Me); 1-phenyl-3-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4c) (1.0 g, 100%), needles, m.p. 161° (lit.,<sup>3</sup> 158°) (Found: C, 66.5; H, 4.9; N, 22.5%;  $M^+$ , 252. Calc. for  $C_{14}H_{12}N_4O$ : C, 66.7; H, 4.8; N, 22.2%;  $M$ , 252);  $\lambda_{\max}$ , 227, 269, and 326 nm ( $\epsilon$  41 950, 36 890, and 42 590);  $\nu_{\max}$ , 1 700  $cm^{-1}$ ;  $\tau$  1.8—2.6 (m, 9 ArH) and 7.53 (s, Me); 1-*p*-chlorophenyl-3-phenyl-1,2,3,4-tetrazolium-5-olate (4d) (1.0 g, 100%), plates, m.p. 190° [Found: C, 56.95; H, 3.4; N, 20.8%;  $M^+$  (<sup>35</sup>Cl), 272.  $C_{13}H_9ClN_4O$  requires C, 57.2; H, 3.3; N, 20.55%;  $M$  (<sup>35</sup>Cl), 272];  $\lambda_{\max}$ , 227, 263, and 328 nm ( $\epsilon$  50 070, 36 810, and 50 760);  $\nu_{\max}$ , 1 700  $cm^{-1}$ ;  $\tau$  1.8—2.6 (m, ArH); 3-*p*-chlorophenyl-1-phenyl-1,2,3,4-tetrazolium-5-olate (4e) (0.9 g, 90%), plates, m.p. 232° [Found: C, 57.4; H, 3.4; N, 20.65%;  $M^+$  (<sup>35</sup>Cl), 272.  $C_{13}H_9ClN_4O$  requires C, 57.2; H, 3.3; N, 20.55%;  $M$  (<sup>35</sup>Cl), 272];  $\lambda_{\max}$ , 228, 267, and 330 nm ( $\epsilon$  76 580, 60 990, and 72 280);  $\nu_{\max}$ , 1 700  $cm^{-1}$ ;  $\tau$  1.8—2.5 (m, ArH).

(b) From potassium arylhydrazonmethanedisulphonates (18). An aqueous solution of benzenediazonium chloride, prepared from aniline (2.1 g), was cooled to  $-5^\circ$  and rapidly poured into a solution of potassium phenylhydrazonmethanedisulphonate (18a) (8.0 g) and potassium hydroxide (2.7 g) in water (150 ml). The deep orange solution was warmed to 50—60° and then kept at room temperature for 5 h. The brown, crystalline precipitate was washed with water and dried. Recrystallisation from ethanol-water and then carbon tetrachloride gave 1,3-diphenyl-1,2,3,4-tetrazolium-5-olate (4a) (1.2 g, 23%), m.p. 157° (lit.,<sup>13</sup> 157°), identical with an authentic sample.

The following compounds were similarly prepared: 1,3-di-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4f) (2.3 g, 39%), needles, m.p. 198° (Found: C, 67.8; H, 5.3; N, 20.9%;  $M^+$ , 266.  $C_{15}H_{14}N_4O$  requires C, 67.7; H, 5.3; N, 21.05%;  $M$ , 266);  $\lambda_{\max}$ , 227, 268, and 331 nm ( $\epsilon$  24 750, 16 760, and 27 180);  $\nu_{\max}$ , 1 700  $cm^{-1}$ ;  $\tau$  1.99 and 2.65 ( $A_2B_2$ ,  $J_{AB}$  9 Hz, *p*-MeC<sub>6</sub>H<sub>4</sub>), 1.99 and 2.69 ( $A_2'B_2'$ ,  $J_{A'B'}$  9 Hz, *p*-MeC<sub>6</sub>H<sub>4</sub>), 7.55 (s, Me), and 7.60 (s, Me); 1,3-di-*p*-chlorophenyl-1,2,3,4-tetrazolium-5-olate (4g) (1.8 g, 26%), plates, m.p. 234° (lit.,<sup>17</sup> 232°) [Found: C, 50.6; H, 2.9; N, 18.1%;  $M^+$  (<sup>35</sup>Cl), 306. Calc. for  $C_{13}H_8Cl_2N_4O$ : C, 50.8; H, 2.6; N, 18.2%;  $M$  (<sup>35</sup>Cl), 306];  $\lambda_{\max}$ , 228, 269, and 333 nm ( $\epsilon$  23 050, 18 620, and 24 150);  $\nu_{\max}$ , 1 700  $cm^{-1}$ ;  $\tau$  1.86 and 2.40 ( $A_2B_2$ ,  $J_{AB}$  9 Hz, *p*-ClC<sub>6</sub>H<sub>4</sub>), and 1.86 and 2.48 ( $A_2'B_2'$ ,  $J_{A'B'}$  9 Hz, *p*-ClC<sub>6</sub>H<sub>4</sub>).

In the manner just described, the disulphonate (18a) (8.0 g) was treated with toluene-*p*-diazonium chloride. Recrystallisation from carbon tetrachloride gave needles (1.6 g) which were shown by mass spectrometry to be a mixture (1 : 1) of 3-phenyl-1-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4b) ( $M^+$ , 252) and 1,3-di-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4f) ( $M^+$ , 266). Similarly, (18a) (8.0 g) and *p*-chlorobenzenediazonium chloride gave a mixture (3 : 2) of 1,3-di-*p*-chlorophenyl-1,2,3,4-tetrazolium-5-olate (4g) [ $M^+$  (<sup>35</sup>Cl), 306] and 1-*p*-chlorophenyl-3-phenyl-1,2,3,4-tetrazolium-5-olate (4d) [ $M^+$  (<sup>35</sup>Cl), 272]; the disulphonate (18c) (8.8 g) and benzenediazonium chloride gave a mixture

(9 : 1) of 3-*p*-chlorophenyl-1-phenyl-1,2,3,4-tetrazolium-5-olate (4e) [ $M^+$  (<sup>35</sup>Cl), 272] and 1,3-diphenyl-1,2,3,4-tetrazolium-5-olate (4a) ( $M^+$ , 238); the disulphonate (18b) (8.2 g) and benzenediazonium chloride gave a mixture (1 : 1) of 1-phenyl-3-*p*-tolyl-1,2,3,4-tetrazolium-5-olate (4c) ( $M^+$ , 252) and 1,3-diphenyl-1,2,3,4-tetrazolium-5-olate (4a) ( $M^+$ , 238).

1,3-Diaryl-5-ethoxy-1,2,3,4-tetrazolium Tetrafluoroborates (9).—1,3-Diphenyl-1,2,3,4-tetrazolium-5-olate (4a) (1.2 g) was added to a solution of triethyloxonium tetrafluoroborate (1.0 g)<sup>18</sup> in dichloromethane (20 ml). After 16 h, ether was added and the crystalline precipitate collected. Recrystallisation from acetone-light petroleum (b.p. 40—60°) gave 5-ethoxy-1,3-diphenyl-1,2,3,4-tetrazolium tetrafluoroborate (9a) (1.6 g, 90%), prisms, m.p. 174° (Found: C, 51.1; H, 4.4; N, 16.0.  $C_{15}H_{15}BF_4N_4O$  requires C, 50.9; H, 4.2; N, 15.8%);  $\lambda_{\max}$ , 215sh, 233infl., and 296 nm ( $\epsilon$  5 820, 4 090, and 10 500);  $\nu_{\max}$ , (KBr) 1 010—1 120br, 1 610, and 1 690  $cm^{-1}$ ;  $\tau$ (CDCl<sub>3</sub> + CF<sub>3</sub>·CO<sub>2</sub>H) 1.8—2.5 (m, 10 ArH), 5.10 (q,  $J$  7 Hz, OCH<sub>2</sub>Me), and 8.48 (t,  $J$  7 Hz, OCH<sub>2</sub>Me);  $m/e$  238 ( $M^+$  — EtBF<sub>4</sub>).

The following compounds were similarly prepared: 1-*p*-chlorophenyl-5-ethoxy-3-phenyl-1,2,3,4-tetrazolium tetrafluoroborate (9d) (1.4 g, 70%), plates, m.p. 159° (Found: C, 46.0; H, 3.7; N, 14.2.  $C_{15}H_{14}BClF_4N_4O$  requires C, 46.4; H, 3.6; N, 14.4%);  $\lambda_{\max}$ , 222 and 304 nm ( $\epsilon$  25 350 and 33 350);  $\nu_{\max}$ , (KBr) 1 030—1 130br, 1 610, and 1 690  $cm^{-1}$ ;  $\tau$ [(CD<sub>3</sub>)<sub>2</sub>CO] 1.7—2.4 (m, 9 ArH), 4.94 (q,  $J$  7 Hz, OCH<sub>2</sub>Me), and 8.40 (t,  $J$  7 Hz, OCH<sub>2</sub>Me);  $m/e$  272 (<sup>35</sup>Cl) ( $M^+$  — EtBF<sub>4</sub>); 3-*p*-chlorophenyl-5-ethoxy-1-phenyl-1,2,3,4-tetrazolium tetrafluoroborate (9e) (1.9 g, 95%), plates, m.p. 180° (Found: C, 46.1; H, 3.8; N, 14.5.  $C_{15}H_{14}BClF_4N_4O$  requires C, 46.4; H, 3.6; N, 14.4%);  $\lambda_{\max}$ , 215(sh), 228infl., and 308 nm ( $\epsilon$  12 500, 8 925, and 22 350);  $\nu_{\max}$ , (KBr) 1 020—1 120br, 1 620, and 1 690  $cm^{-1}$ ;  $\tau$ [(CD<sub>3</sub>)<sub>2</sub>CO] 1.6—2.3 (m, 9 ArH), 4.95 (q,  $J$  7 Hz, OCH<sub>2</sub>Me), and 8.40 (t,  $J$  7 Hz, OCH<sub>2</sub>Me);  $m/e$  272 (<sup>35</sup>Cl) ( $M^+$  — EtBF<sub>4</sub>); 5-ethoxy-1,3-di-*p*-tolyl-1,2,3,4-tetrazolium tetrafluoroborate (9f) (2.0 g, 100%), plates, m.p. 138° (Found: C, 53.3; H, 5.3; N, 14.5.  $C_{17}H_{18}BF_4N_4O$  requires C, 53.4; H, 5.0; N, 14.7%);  $\lambda_{\max}$ , 218, 233infl., and 313 nm ( $\epsilon$  9 980, 6 270, and 16 650);  $\nu_{\max}$ , (KBr) 1 020—1 120br, 1 610, and 1 690  $cm^{-1}$ ;  $\tau$  2.04 and 2.68 ( $A_2B_2$ ,  $J_{AB}$  9 Hz, *p*-MeC<sub>6</sub>H<sub>4</sub>), 2.30 and 2.68 ( $A_2'B_2'$ ,  $J_{A'B'}$  9 Hz, *p*-MeC<sub>6</sub>H<sub>4</sub>), 5.11 (q,  $J$  7 Hz, OCH<sub>2</sub>Me), 7.59 (s, 2 × Me), and 8.50 (t,  $J$  7 Hz, OCH<sub>2</sub>Me);  $m/e$  266 ( $M^+$  — EtBF<sub>4</sub>); 1,3-di-*p*-chlorophenyl-5-ethoxy-1,2,3,4-tetrazolium tetrafluoroborate (9g) (1.9 g, 92%), plates, m.p. 169° (Found: C, 42.6; H, 3.4; N, 13.4.  $C_{15}H_{13}BCl_2F_4N_4O$  requires C, 42.6; H, 3.1; N, 13.2%);  $\lambda_{\max}$ , 220 and 311 nm ( $\epsilon$  16 920 and 20 250);  $\nu_{\max}$ , (KBr) 1 020—1 100br, 1 620, and 1 690  $cm^{-1}$ ;  $\tau$ (CDCl<sub>3</sub> + CF<sub>3</sub>·CO<sub>2</sub>H) 1.8—2.5 (m, 8 ArH), 5.05 (q,  $J$  7 Hz, OCH<sub>2</sub>Me), and 8.44 (t,  $J$  7 Hz, OCH<sub>2</sub>Me);  $m/e$  306 (<sup>35</sup>Cl) ( $M^+$  — EtBF<sub>4</sub>).

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