Cyclic Meso-ionic Compounds. Part XI.[1] Synthesis, Spectroscopic Properties, and Chemistry of 1,3,4-Triazolium-2-aminides

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A new route to the meso-ionic 1,3,4-triazolium-2-aminides (I) is reported, yielding a number of derivatives including pairs of structural isomers of the types (I) and (II). Their physical properties and chemical reactions are discussed, including the isomerisation (I) ⟶ (II).

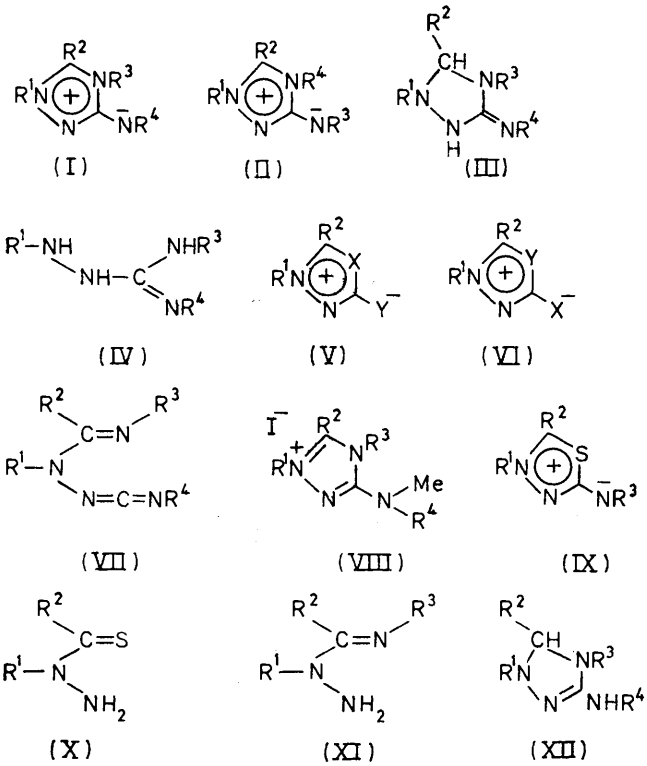
1,3,4-Triazolium-2-aminides (I) were first prepared by Busch and his co-workers,[2] who represented them by a stereochemically impossible bicyclic structure. Later, Schönberg,[3] reinterpreted the physical and chemical properties in terms of a zwitterionic structure. Baker and Ollis [4] subsequently pointed out that these heterocycles belonged to the general class of meso-ionic compounds (V) and could be represented by structure (I). The 1,3,4-triazolium-2-aminides (I) can be prepared either directly by the reaction of an aminoguanidine (IV) with an acid chloride, or by condensation of the aminoguanidine (IV) with an aldehyde to give a triazolidine (III), which can be oxidised to the 1,3,4-triazolium-2-aminide (I).[2] The triphenyl derivative (Ia) is well known as the nitrate precipitant, 'nitron.' [5] Synthesis of compounds (I) from aminoguanidines (IV) is unsatisfactory if the groups R^3 and R^4 are different, because this leads to a mixture of isomers (I) and (II). For example, in the condensation of diphenyl-*p*-tolylaminoguanidine (IVb) with formaldehyde, Busch and Mehrtens [2] recognised that the product was probably a mixture of the triazolidines (IIIb and c) which would lead to a mixture of 1,3,4-triazolium-2-aminides (Ib and IIb). Our interest [1] in the preparation and interconversion of pairs of meso-ionic isomers of the general types (V) and (VI) has encouraged us to look for methods for the specific synthesis of isomeric 1,3,4-triazolium-2-aminides of the types (I) and (II). We now report [6] a new method for the synthesis of the 1,3,4-triazolium-2-aminides (I).

In the preceding paper,[1] the synthesis of 1,3,4-thiadiazolium-2-aminides (IX) by the condensation of *N*-thioacylhydrazines (X) with isocyanide dichlorides was reported; it was expected that a similar reaction between *N*-aminobenzamidines (XI; R^2 = Ph) and isocyanide dichlorides would give the 1,3,4-triazolium-2-aminides (I) corresponding to the tautomeric carbodiimides (VII). The preparation of *N*-amino-*NN'*-diphenylbenzamidine (XIq) and *N*-amino-*N*-methyl-*N'*-phenylbenzamidine (XIr) by the condensation of *N*-phenylbenzimidoyl chloride with phenylhydrazine and methylhydrazine, respectively, has recently been described.[7] By this method, we have also prepared the compounds (XIs—v). Isocyanide dichlorides are prepared by treatment of isothiocyanates with chlorine.[8]

When equivalent amounts of *N*-amino-*N*-methyl-*N'*-phenylbenzamidine (XIr) and phenyl isocyanide dichloride in toluene were heated under reflux, hydrogen chloride was evolved. Evaporation gave a chloride which on treatment with aqueous ammonia gave yellow

[1] Part X, W. D. Ollis and C. A. Ramsden, preceding paper.
[2] M. Busch, *Ber.*, 1905, **38**, 856; M. Busch and G. Mehrtens, *ibid.*, p. 4049; M. Busch, H. Brandt, and G. Blume, *J. prakt. Chem.*, 1906, **74**, 533.
[3] A. Schönberg, *J. Chem. Soc.*, 1938, 824.
[4] W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.
[5] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 3rd edn., 1962, p. 131.
[6] W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1224.
[7] K. T. Potts, S. K. Roy, and D. P. Jones, *J. Heterocyclic Chem.*, 1965, **2**, 105; *J. Org. Chem.*, 1967, **32**, 2245.
[8] E. Kühle, B. Anders, and G. Zumach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 649; E. Kühle, B. Anders, and G. Zumach, in 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic Press, New York, 1971, **6**, 127.

prisms of 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-anilide (Id). In a similar way, compounds (Ie—p) were synthesised in *ca.* 60% yield. The products (I) are yellow, crystalline compounds which usually melt above



In formulae (I)—(XII):

a; $R^1 = R^3 = R^4 = Ph$, $R^2 = H$
b; $R^1 = R^3 = Ph$, $R^2 = H$, $R^4 = p\text{-}MeC_6H_4$
c; $R^1 = R^4 = Ph$, $R^2 = H$, $R^3 = p\text{-}MeC_6H_4$
d; $R^1 = Me$, $R^2 = R^3 = R^4 = Ph$
e; $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = p\text{-}MeC_6H_4$
f; $R^1 = Me$, $R^2 = R^4 = Ph$, $R^3 = p\text{-}MeC_6H_4$
g; $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = p\text{-}MeC_6H_4$
h; $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = p\text{-}ClC_6H_4$
j; $R^1 = Me$, $R^2 = R^4 = Ph$, $R^3 = p\text{-}ClC_6H_4$
k; $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = p\text{-}ClC_6H_4$
m; $R^1 = Me$, $R^2 = R^4 = Ph$, $R^3 = p\text{-}MeO{\cdot}C_6H_4$
n; $R^1 = R^4 = R^3 = R^4 = Ph$
p; $R^1 = R^2 = R^3 = Ph$, $R^4 = p\text{-}ClC_6H_4$
q; $R^1 = R^2 = R^3 = Ph$
r; $R^1 = Me$, $R^2 = R^3 = Ph$
s; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-}MeC_6H_4$
t; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-}ClC_6H_4$
u; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-}MeO{\cdot}C_6H_4$
v; $R^1 = R^2 = Ph$, $R^3 = p\text{-}ClC_6H_4$

200°, often with decomposition. They are only slightly soluble in benzene, but readily soluble in chloroform or ethanol.

Their i.r. spectra show strong absorption in the region 1550—1560 cm^{-1}, which can be attributed to C=N stretching; *cf.* the corresponding thiadiazoles (IX) (1550—1580 cm^{-1}).[1] The i.r. spectra of compounds (Id—p) show no sign of N–H absorption bands nor of a carbodi-imide stretching vibration (2130—2155 cm^{-1}). The dipole moments[9] of compounds (Id) (8·2 D), (Ih) (9·9 D), (Ij) (8·2 D), and (Ik) (9·8 D) in benzene solution have been measured and are in excellent agreement with the proposed meso-ionic structures. A detailed analysis of these dipole moments will be published.[10]

The n.m.r. and u.v. spectra of the 1,3,4-triazolium-2-aminides (I) are similar to those of other meso-ionic systems of the general type (V).[1,11] Mass spectrometry has proved to be an almost indispensable tool in the study of the isomers (I) and (II). For example, although the isomers (If) and (IIf) are almost identical in their physical and chemical properties, mass spectrometry easily distinguishes between them. Both compounds give a molecular ion at *m/e* 340, but the isomer (If) gives a fragment ion at *m/e* 194 [$PhC{\equiv}\overset{+}{N}{-}C_6H_4Me(p)$], whereas (IIf) gives a fragment ion at *m/e* 180 ($PhC{\equiv}\overset{+}{N}Ph$); other pairs of isomers are equally readily distinguished. An examination of the mass spectra of the isomers (I) and (II) together with the mass spectra of other meso-ionic systems of the general types (V) and (VI) will be reported.[12]

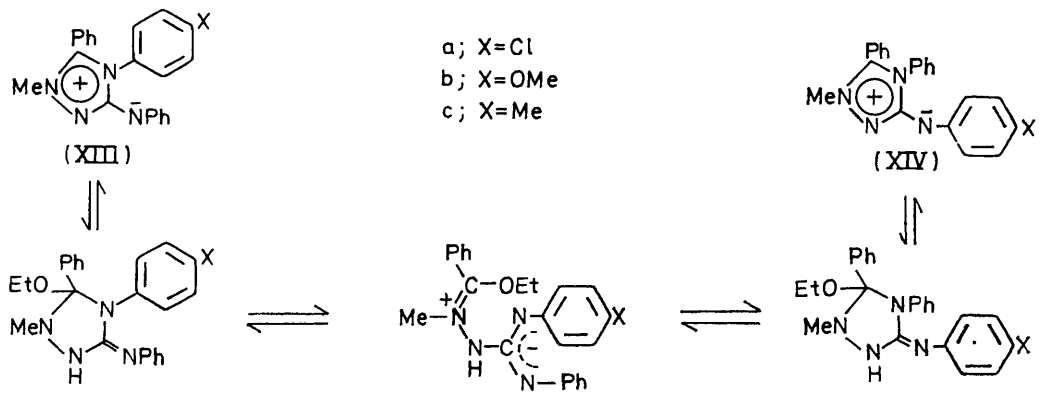
We have discussed two examples of the rearrangement (V) ⟶ (VI) of meso-ionic systems catalysed by ethanol:[1,11] we now report a third example, interconversion of the 1,3,4-triazolium-2-aminides (XIII) and (XIV). The suggested mechanism (Scheme) of this rearrangement (XIII) ⟶ (XIV) is analogous to that which we have proposed for similar rearrangements of the general type (V) ⟶ (VI). This may be recognised as involving a betaine intermediate or its cationoid equivalent.

It is assumed that the interconversion between the meso-ionic isomers (I) and (II) in boiling ethanol takes place under equilibration conditions. An impression of the relative stabilities of the meso-ionic isomers can therefore be acquired by considering the position of the equilibrium (XIII) ⇌ (XIV). This has been investigated by boiling ethanolic solutions of each of the compounds (XIIIa—c) and (XIVa and c). The chloro-compound (XIIIa) is quantitatively transformed into (XIVa) and under similar conditions (XIVa) is unchanged. The *p*-methoxy-derivative (XIIIb) is recovered from boiling ethanol. We have been unable to study the isomer (XIVb) because of our failure to prepare *p*-methoxyphenyl isocyanide dichloride.[13] The *p*-tolyl derivatives (XIIIc) and (XIVc) when separately heated in ethanol gave an equilibrium mixture which by mass spectrometric examination was shown to have 1 : 1 composition. These facts are relevant to a consideration of the relative thermodynamic stabilities of isomers of the types (XIII) and (XIV). However, in our view, an acceptable interpretation of these results in terms of an

[9] K. A. Jensen and A. Friediger, *Kgl. danske Videnskab. Selskab., Mat.-fys. Medd.*, 1943, **20**, 1; F. L. Warren, *J. Chem. Soc.*, 1938, 1100.
[10] W. D. Ollis, C. A. Ramsden, and L. E. Sutton, to be published.
[11] Part IX, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 627.
[12] Part XIII, W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 645.
[13] G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 1940, 191.

electronic influence of the substituent (X = Cl, OMe, or Me) is not yet possible.

The reaction of the 1,3,4-triazolium-2-aminides (I) with mineral acids and alkyl halides to form salts was described by Busch.[2] We have found that compound (Id) reacts with dilute nitric acid to form a nitrate and with methyl iodide to form the 1,3,4-triazolium iodide (VIIId). The observation that the isomers (XIIIa) and (XIVa) react with methyl iodide to form the distinct iodides (VIIIj) (m.p. 188—189°) and (VIIIh) (m.p. 176—178°), respectively, is of particular interest.



SCHEME

The 1,3,4-triazolium-2-aminides (I) can be reduced to 1,3,4-triazolidines (III) by lithium aluminium hydride in hot dioxan. For example, the two *p*-chlorophenyl isomers (XIIIa) and (XIVa) gave the 1,3,4-triazolidines (IIIj) (m.p. 148—149°) and (IIIh) (m.p. 161—162°), respectively. The triazolidines (III) may be equally well formulated as the tautomeric triazolines (XII).

EXPERIMENTAL

General experimental directions are given in Part VIII.[14]

Preparation of N-*Aminobenzamidines* (XI; R^2 = Ph).—By the procedure described by Potts, Roy, and Jones,[7] the following *N*-aminobenzamidines (XI) have been prepared: N-*amino*-N-*methyl*-N′-p-*tolylbenzamidine* (XIs) (36%), crystallised from light petroleum (b.p. 80—100°), prisms, m.p. 93—94° (Found: C, 75·6; H, 7·2; N, 17·6. $C_{15}H_{17}N_3$ requires C, 75·3; H, 7·1; N, 17·6%); $\nu_{max.}$ 1580 and 1600 cm^{-1}; τ 2·6—3·0 (m, C_6H_5), τ_A 3·16, τ_B 3·55 [A_2B_2 system, J_{AB} 7 Hz (*p*-tolyl)], τ 5·46br (s, NH_2) and 7·04 (s, NMe); N-*amino*-N′-p-*chlorophenyl*-N-*methylbenzamidine* (XIt) (29%), crystallised from light petroleum (b.p. 80—100°), prisms, m.p. 97—98° (Found: C, 65·0; H, 5·4; Cl, 13·8; N, 16·1. $C_{14}H_{14}ClN_3$ requires C, 64·7; H, 5·4; Cl, 13·7; N, 16·2%); $\nu_{max.}$ 1580 and 1600 cm^{-1}; τ 2·6—3·1 (m, C_6H_5), τ_A 3·03, τ_B 3·52 [A_2B_2 system, J_{AB} 8 Hz (*p*-ClC_6H_4)], τ 5·37br (s, NH_2) and 7·04 (s, NMe); N-*amino*-N′-p-*chlorophenyl*-N-*phenylbenzamidine* (XIv) (12%), crystallised from ethanol, needles, m.p. 133—134° (Found: C, 70·5; H, 4·7; Cl, 10·9; N, 12·9%; M^+, 321. $C_{19}H_{16}ClN_3$ requires C, 70·9; H, 5·0; Cl, 11·0; N, 13·1%; *M*, 321); $\nu_{max.}$ 1575 cm^{-1}; τ 2·8—3·1 (m, 10 aromatic H), τ_A 2·91, τ_B 3·44 [A_2B_2 system, J_{AB} 8 Hz (*p*-ClC_6H_4)], τ 5·2br (s, NH_2).

[14] Part VIII, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624.

Preparation of 1,3,4-*Triazolium*-2-*aminides* (I).—A solution of phenyl isocyanide dichloride[15] (3·9 g) in toluene (10 ml) was added dropwise (10 min) with stirring under reflux to a solution of *N*-amino-*N*-methyl-*N*′-phenylbenzamidine[7] (XIr) (5·0 g) in toluene (40 ml). After further boiling (30 min), the toluene was removed by evaporation giving a dark residue which was dissolved in chloroform (50 ml). The solution was extracted with aqueous 2% acetic acid (3 × 150 ml) and the combined acid extracts were basified with ammonium hydroxide. A bright yellow colouration immediately developed and the solution was extracted with chloroform (3 × 200 ml). The combined chloroform extracts, after washing with water (200 ml) and drying ($MgSO_4$), were evaporated, giving a yellow residue which was crystallised from chloroform–ether. Two recrystallisations gave 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-*anilide* (Id) (5·0 g, 69%), yellow prisms, m.p. 218° (decomp.) (Found: C, 77·3; H, 5·7; N, 17·4%; M^+, 326. $C_{21}H_{18}N_4$ requires C, 77·3; H, 5·6; N, 17·2%; *M*, 326); $\lambda_{max.}$ 249 nm (ε 21,900); $\nu_{max.}$ 1555 cm^{-1}; τ 2·4—3·0 (m, 15 aromatic H) and 6·35 (s, NMe).

The following compounds were similarly prepared from the appropriate *N*-aminoamidine (XI) (1·0 g) and an equimolar amount of the appropriate isocyanide dichloride,[1,8] with toluene (15—25 ml) as solvent: 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-p-*toluidide* (Ie) (0·91 g, 60%), pale yellow needles, m.p. 220—221° (from chloroform–ether) (Found: C, 77·3; H, 5·7; N, 16·3%; M^+, 340. $C_{22}H_{20}N_4$ requires C, 77·6; H, 5·9; N, 16·5%; *M*, 340); $\lambda_{max.}$ 250 nm (ε 20,400); $\nu_{max.}$ 1560 cm^{-1}; τ 2·5—3·0 (m, 14 aromatic H), 6·28 (s, NMe), and 7·75 (s, Me); 4-*methyl*-5-*phenyl*-1-p-*tolyl*-1,3,4-*triazolium*-2-*anilide* (If) (0·95 g, 67%), pale yellow prisms, m.p. 229° (decomp.) (from chloroform–ether) (Found: C, 77·4; H, 5·9; N, 16·3%; M^+, 340. $C_{22}H_{20}N_4$ requires C, 77·6; H, 5·9; N, 16·5%; *M*, 340); $\lambda_{max.}$ 249 nm (ε 24,300); $\nu_{max.}$ 1550 cm^{-1}; τ 2·4—3·0 (m, 14 aromatic H), 6·25 (s, NMe), and 7·72 (s, Me); 4-*methyl*-5-*phenyl*-1-p-*tolyl*-1,3,4-*triazolium*-2-p-*toluidide* (Ig) (71%), yellow needles, m.p. 198—199° (from chloroform–ether) (Found: M^+, 354·1838. $C_{23}H_{22}N_4$ requires *M*, 354·1842); $\lambda_{max.}$ 250 nm (ε 26,200); $\nu_{max.}$ 1550 cm^{-1}; τ 2·0—3·0 (m, 13 aromatic H), 6·11 (s, NMe), 7·58 (s, Me), and 7·64 (s, Me); 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-p-*chloroanilide* (Ih) (0·91 g, 57%), yellow rods, m.p. 224° (from chloroform–ether) [Found: C, 69·9; H, 4·75; Cl, 10·0; N, 15·8%;

[15] R. S. Bly, G. A. Perkins, and W. L. Lewis, *J. Amer. Chem. Soc.*, 1922, **44**, 2896.

M^+, 360 (^{35}Cl). $C_{21}H_{17}ClN_4$ requires C, 69·9; H, 4·7; Cl, 9·85; N, 15·5%; M, 360 (^{35}Cl)]; $\lambda_{max.}$ 256 and 288 nm (ε 29,100 and 14,900); $\nu_{max.}$ 1550 cm^{-1}; τ 2·5—3·0 (m, 4 aromatic H) and 6·25 (s, NMe); 1-p-*chlorophenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-*anilide* (Ij) (0·74 g, 53%), yellow prisms, m.p. 231° (decomp.) (from chloroform–ether) [Found: C, 69·6; H, 4·6; Cl, 10·0; N, 15·8%; M^+, 360 (^{35}Cl). $C_{21}H_{17}ClN_4$ requires C, 69·9; H, 4·7; Cl, 9·85; N, 15·5%; M, 360 (^{35}Cl)]; $\lambda_{max.}$ 220 and 247 nm (ε 21,000 and 22,400); $\nu_{max.}$ 1550 cm^{-1}; τ 2·4—3·0 (m, 14 aromatic H) and 6·30 (s, NMe); 1-p-*chlorophenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-p-*chloroanilide* (Ik) (0·88 g, 58%), yellow prisms, m.p. 231° (decomp.) (from chloroform–ether) [Found: C, 63·5; H, 3·9; Cl, 17·8; N, 14·2%; M^+, 394 (^{35}Cl). $C_{21}H_{16}Cl_2N_4$ requires C, 63·8; H, 4·05; Cl, 18·0; N, 14·2%; M, 394 (^{35}Cl)]; $\lambda_{max.}$ 255 and 287 nm (ε 23,200 and 17,600); $\nu_{max.}$ 1550 cm^{-1}; τ 2·4—3·0 (m, 13 aromatic H) and 6·26 (s, NMe); 1-p-*methoxyphenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-*anilide* (Im) (0·77 g, 55%), yellow feathers, m.p. 230° (decomp.) (from chloroform–ether) (Found: C, 73·9; H, 5·4; N, 15·6%; M^+, 356. $C_{22}H_{20}N_4O$ requires C, 74·0; H, 5·7; N, 15·7%; M, 356); $\lambda_{max.}$ 235 and 249 nm (ε 23,200 and 26,600); $\nu_{max.}$ 1550 cm^{-1}; τ ($CDCl_3$–CF_3·CO_2H) 2·3—3·2 (m, 14 aromatic H), 6·05 (s, NMe), and 6·20 (s, OMe).

1,4,5-*Triphenyl*-1,3,4-*triazolium*-2-*anilide* (In).—A solution of *N*-amino-*NN'*-diphenylbenzamidine [7] (XIq) (2·0 g) and phenyl isocyanide dichloride [15] (1·2 g) in toluene (25 ml) was heated under reflux (1 h) with stirring. After cooling, the solvent was decanted and the solid residue was dissolved in chloroform (50 ml). Dry ammonia was passed through the chloroform solution (2 min), which was then filtered, and the filtrate was evaporated. The residue was crystallised from benzene and recrystallised from chloroform–ether giving the product (In) (1·05 g, 39%), yellow needles, m.p. 233—234° (decomp.) (lit.,[2] 231—232°) (Found: C, 80·6; H, 5·3; N, 14·5%; M^+, 388. Calc. for $C_{26}H_{20}N_4$: C, 80·4; H, 5·15; N, 14·4%; M, 388); $\lambda_{max.}$ 249 and 290sh (ε 29,200 and 7150); $\nu_{max.}$ 1560 cm^{-1}; τ 2·61 (m, aromatic H).

In the same way, *N*-amino-*NN'*-diphenylbenzamidine [7] (XIq) (1·0 g) and *p*-chlorophenyl isocyanide dichloride [8] (0·73 g) in toluene (20 ml) gave 1,4,5-*triphenyl*-1,3,4-*triazolium*-2-p-*chloroanilide* (Ip) (0·18 g, 12%), orange needles, m.p. 245° (from chloroform–ether) [Found: C, 73·7; H, 4·7; Cl, 8·6; N, 13·1%; M^+, 422 (^{35}Cl). $C_{26}H_{19}ClN_4$ requires C, 73·9; H, 4·5; Cl, 8·4; N, 13·25%; M, 422 (^{35}Cl)]; $\lambda_{max.}$ 256, 291, and 386 nm (ε 23,200, 14,600, and 1300); $\nu_{max.}$ 1560 cm^{-1}; τ 2·2—3·1 (m, aromatic H).

Equilibration of 1-p-*Chlorophenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-*anilide* (Ij).—A solution of compound (Ij) (1·0 g) in absolute ethanol (50 ml) was heated under reflux (2 days). After cooling and concentration, ether was added and the crystalline product collected giving 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-*p*-chloroanilide (Ih) (0·78 g, 78%), m.p. 223—224°, identical with an authentic sample (see above).

Equilibration of 4-*Methyl*-5-*phenyl*-1-p-*tolyl*-1,3,4-*triazolium*-2-*anilide* (If) *and* 4-*Methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-p-*toluidide* (Ie).—Compound (If) (0·5 g) was heated under reflux (5 days) in absolute ethanol (30 ml). The ethanol was removed by evaporation and the crystalline residue, analysed by mass spectrometry, was shown to be an approximately 50 : 50 mixture of isomers (If) and (Ie); *m/e* 340 ($M^{\cdot+}$), 180 ($PhC{\equiv}\overset{+}{N}Ph$), and 194 ($PhC{\equiv}\overset{+}{N}{-}C_6H_4Me$-*p*). The crystalline residue was redissolved in ethanol and heated under reflux (7 days). No change in the composition of the mixture was observed. The same mixture was obtained when the isomer (Ie) (0·5 g) was heated under reflux (14 days) in absolute ethanol (30 ml).

Equilibration of 1-p-*Methoxyphenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-*anilide* (Im).—Compound (Im) (0·5 g), heated under reflux (2 days) in absolute ethanol (50 ml), was recovered unchanged.

1,3,4-*Triazolium Methiodides* (VIII).—4-Methyl-1,5-diphenyl-1,3,4-triazolium-2-anilide (Id) (0·5 g) and methyl iodide (1·0 g) were heated under reflux (2 h) in benzene (25 ml). The benzene was evaporated off and the residual oil was crystallised from water (*ca.* 100 ml). Recrystallisation gave 4-*methyl*-2-N-*methylanilino*-1,5-*diphenyl*-1,3,4-*triazolium iodide* (VIIId) (0·45 g, 62%), cubes, m.p. 170—171° (Found: C, 56·4; H, 4·55; N, 11·9. $C_{22}H_{21}IN_4$ required C, 56·4; H, 4·5; N, 12·0%); $\nu_{max.}$ 1560 cm^{-1}; τ 1·8—3·1 (m, 15 aromatic H), 5·91 (s, NMe), and 6·50 (s, NMe); *m/e* 326 ($M^{\cdot+}$ — MeI).

The following compounds were similarly prepared from the corresponding meso-ionic 1,3,4-triazole (I) (0·5 g) and methyl iodide in benzene: 2-p-*chloro*-N-*methylanilino*-4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium iodide* (VIIIh) (0·40 g, 57%), needles, m.p. 176—178° (from water) (Found: C, 52·75; H, 3·9; N, 10·9. $C_{22}H_{20}ClIN_4$ requires C, 52·5; H, 4·0; N, 11·1%); $\nu_{max.}$ 1570 cm^{-1}; τ 1·9—3·1 (m, 14 aromatic H), 5·94 (s, NMe), and 6·50 (s, NMe); *m/e* 360 ($M^{\cdot+}$ — MeI) (^{35}Cl); 1-p-*chlorophenyl*-4-*methyl*-2-N-*methylanilino*-5-*phenyl*-1,3,4-*triazolium iodide* (VIIIj) (0·50 g, 71%), needles, m.p. 188—189° (from water) (Found: C, 52·7; H, 4·2; N, 10·9. $C_{22}H_{20}ClIN_4$ requires C, 52·5; H, 4·0; N, 11·1%); $\nu_{max.}$ 1560 cm^{-1}; τ 1·8—3·1 (m, 14 aromatic H), 5·95 (s, NMe), and 6·47 (s, NMe); *m/e* 360 ($M^{\cdot+}$ — MeI) (^{35}Cl).

2-*Anilino*-4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium Nitrate*.—4-Methyl-1,5-diphenyl-1,3,4-triazolium-2-anilide (Id) (1·0 g) was heated with 2N-nitric acid. Ethanol was added and crystallisation yielded the 1,3,4-*triazolium nitrate* (0·72 g, 60%), plates, m.p. 218—219° (Found: C, 64·8; H, 4·6; N, 17·7. $C_{21}H_{19}N_5O_3$ requires C, 64·8; H, 4·85; N, 18·0%); $\nu_{max.}$ (KBr) 1570 cm^{-1}; τ ($CDCl_3$–CF_3·CO_2H) 2·0—3·0 (m, 15 aromatic H) and 5·96 (d, *J* 8 Hz, Me); *m/e* 326 ($M^{\cdot+}$ — HNO_3).

1,3,4-*Triazolidines* (III).—4-Methyl-1,5-diphenyl-1,3,4-triazolium-2-anilide (Id) (1·0 g) in dry dioxan (20 ml) was heated under reflux. Lithium aluminium hydride (0·1 g) was added and the mixture was stirred until the solution became colourless (5 min). After cooling, the excess of lithium aluminium hydride was destroyed by adding water (25 ml), dropwise at first, and inorganic residues were dissolved by adding a minimal volume of 2N-sodium hydroxide. The aqueous solution was extracted with chloroform (3 × 30 ml) and the combined chloroform extracts were washed with water (25 ml) and dried ($MgSO_4$). Evaporation gave a colourless oil which was crystallised from ether and recrystallised from chloroform–ether giving 2-*anilino*-4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolidine* (IIId) (0·55 g, 55%), prisms, m.p. 159—160° (Found: C, 77·1; H, 6·2; N, 16·8%; M^+, 328. $C_{21}H_{20}N_4$ requires C, 76·8; H, 6·1; N, 17·1%; M, 328); $\nu_{max.}$ 1530 cm^{-1}; τ 2·4—3·2 (m, 15 aromatic H), 4·65br (s, NH), 5·0 (s, CH), and 7·33 (s, NMe).

The following compounds were similarly prepared from the corresponding meso-ionic 1,3,4-triazole (I) (1·0 g) and

lithium aluminium hydride in dioxan: 2-p-*chloroanilino*-4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolidine* (IIIh) (0·65 g, 65%), prisms, m.p. 161—162° (from chloroform–ether) [Found: C, 69·8; H, 5·1; N, 15·2%; M^+, 362 (^{35}Cl). $C_{21}H_{19}ClN_4$ requires C, 69·5; H, 5·2; N, 15·45%; *M*, 362 (^{35}Cl)]; $\nu_{max.}$ 1540 cm^{-1}; τ 2·3—3·0 (m, 14 aromatic H), 4·52br (s, NH), 4·96 (s, CH), and 7·30 (s, NMe); 2-*anilino*-1-p-*chlorophenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolidine* (IIIj) (0·63 g, 63%), prisms, m.p. 148—149° (from chloroform–ether) [Found: C, 69·3; H, 5·3; N, 15·2%; M^+, 362 (^{35}Cl). $C_{21}H_{19}ClN_4$ requires C, 69·5; H, 5·2; N, 15·4%; *M*, 362 (^{35}Cl)]; $\nu_{max.}$ 1540 cm^{-1}; τ 2·3—3·1 (m, 14 aromatic H), 4·57br (s, NH), 5·04 (s, CH), and 7·30 (s, NMe).

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