Reaction of Benzonitrile *N*-(*p*-Nitrophenyl)imide with 5-Substituted Tetrazoles: A New Route to Substituted 1,2,4-Triazoles *via* *N*-Hydrazonoyltetrazoles

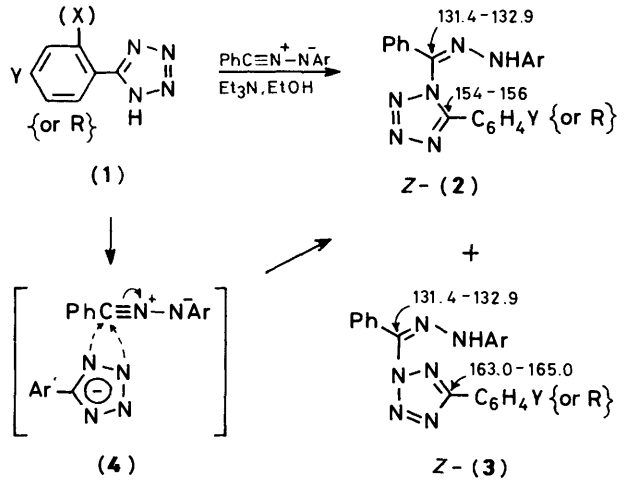
Richard N. Butler* and Kevin J. Fitzgerald
Chemistry Department, University College, Galway, Ireland

A wide range of phenyl 5-R-substituted (R = aryl, alkyl, amino, halo, H) 1- and 2-hydrazonoyltetrazoles has been synthesized. Substituent effects on the orientation of nitrile imide attack on 5-aryltetrazoles are reported. Thermolysis and fragmentation of the resulting hydrazonoyltetrazoles under different conditions gave high yields of a range of substituted 1,2,4-triazoles including aryl, alkyl, amino and azido derivatives. Interesting substituent effects including steric blocking of triazole formation from 5-aryltetrazoles by di-*ortho*-substitution of the 5-aryl ring are also noted.

While tetrazoles have been treated with a variety of electrophilic reagents[1-3] little is known of their reactions with electrophilic 1,3-dipoles, the only report[4] being that of the reaction of 5-phenyl- and 5-isopropyl-tetrazole with nitrile oxides to give mixtures of 1- and 2-oximinotetrazoles. These fragmented when heated to give 1,2,4-oxadiazoles.[4] Herein we report[5] the reactions of a wide range of 5-substituted tetrazoles with the 1,3-dipole, benzonitrile *N*-(*p*-nitrophenyl)imide, along with interesting and useful reactions of the resulting hydrazonoyltetrazoles.

Results and Discussion

N-Hydrazonoyltetrazoles.—A series of the substituted 5-aryltetrazoles (**1**) was allowed to react with benzonitrile *N*-(*p*-nitrophenyl)imide by treating a mixture of the tetrazole and *N*-*p*-nitrophenylbenzohydrazonoyl bromide with 2 mol equiv. of triethylamine in benzene under reflux. The products were mixtures of the new hydrazonoyltetrazoles (**2**) and (**3**) respectively (Table). Such stable tetrazoles with iminyl substituents on nitrogen are rare.[1-3,6,7] The products (**2**) and (**3**) were pure single isomers and we assume they have the *Z*-structure shown (Scheme 1). This is consistent with subsequent



Scheme 1. Ar = *p*-$C_6H_4NO_2$ [some ^{13}C shift ranges in $(CD_3)_2SO$] Y,(X) = **a**, *p*-MeO; **b**, *p*-Me; **c**, H; **d**, *p*-Cl; **e**, *p*-Br; **f**, *p*-NO_2; **g**, *o*-Me; **h**, *o*-Cl; **i**, *o*,*o*-Cl_2. R = **j**, NH_2; **k**, $NHCH_2Ph$; **l**, Me; **m**, H; (*n*) Cl

Table. Products[a]

Part I: Hydrazonoyltetrazoles (Scheme 1)

Compd.	M.p. (°C)	Yield (%)	Compd.	M.p. (°C)	Yield (%)	K_{T_c} (2)/(3) Isolated	K_{T_c} (2)/(3) ^{13}C n.m.r.[e]
(**2a**)	188	51	(**3a**)	177	40	1.27	1.27
(**2b**)	146—148	50	(**3b**)	163—164	42	1.19	1.24
(**2c**)	215—217[b]	49	(**3c**)	138	45	1.08	1.14
(**2d**)	161—162[b]	46	(**3d**)	145—146	47	0.97	1.02
(**2e**)	163[b]	47	(**3e**)	158	51	0.92	0.95
(**2f**)	180[b]	37	(**3f**)	205	58	0.63	0.60
(**2g**)	226	55	(**3g**)	211	35	1.57	
(**2h**)	205[b]	47	(**3h**)	197—198	40	1.18	
(**2i**)	190—192[b]	47	(**3i**)	211	40	1.18	
(**2j**)	283—284	80	(**3j**)	*d*			
(**2k**)	146—147	84	(**3k**)	*d*			
(**2l**)	209[b]	46	(**3l**)	173—174	22		
(**2m**)	*c*		(**3m**)				
(**2n**)	*c*		(**3n**)				

Part II: Substituted 1,2,4-triazoles (Schemes 2 and 3)

From (**2**)			From (**3**)		
(7; R′ = H)	292—294	89	(**15b**)	252—253[f]	89
(7; R′ = $PhCH_2$)	159—160	87	(**15c**)	224[f]	65
(**9m**)	200—201	60	(**15d**)	154—155[f]	74
(**11**)	166	35	(**15h**)	215—217[f]	81
(**9a**)	185[b]	82	(**15i**)	228[g]	87
(**9b**)	176—177[b]	84			
(**9c**)	159—160[b]	90			
(**9d**)	201—202[b]	86			
(**9e**)	203[b]	77			
(**9f**)	224—225	80			
(**9g**)	178[b]	84			
(**9h**)	173—174[b]	84			
(**9l**)	139—140[b]	75			

[a] Products were recrystallised from aqueous alcohol except where stated otherwise. [b] Recrystallised from aqueous acetic acid. [c] Too unstable to be isolated. Products were (**9m**) and (**11**) Part II. [d] Not encountered. [e] Measured by direct analysis of the product mixture prior to separation and work-up; the ratios are the average ratio of three signals for each pair, tetrazole C-5 and *p*-nitrophenyl C-2′ and C-3′. [f] Recrystallised from hexanol–light petroleum (b.p. 40—60 °C). [g] From chloroform.

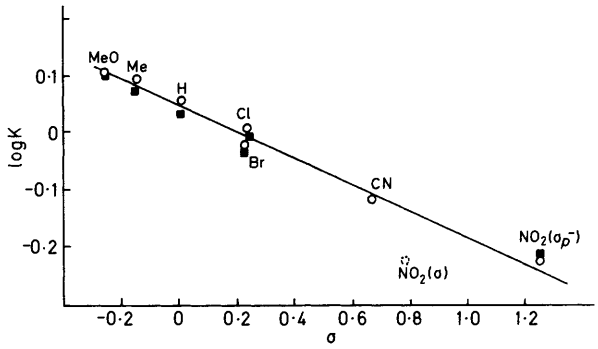
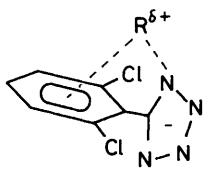


Figure. Plot of log K_{T_e} (Table) *vs.* substituent Hammett σ value (from L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill Kogakusha Ltd., Tokyo, 1970, p. 356). NO_2 required σ_p^- for best fit. ○ from n.m.r. analysis of isomers ■ from isolation of isomers

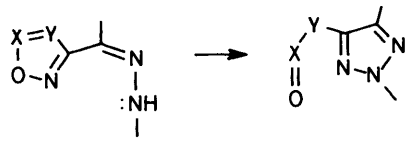
reactions of compounds (**2**), it having been established[8] that nitrilium ions and nitrile oxides react stereospecifically with nuclophiles to give the product in which the incoming nucleophile and the developing lone pair on the adjacent nitrogen are *trans*. The distribution of the products (Table) was established by careful isolation and also by direct *in situ* ^{13}C n.m.r. analysis of the reaction solution prior to work-up. The product ratios so obtained were in good agreement and showed a linear relationship with the Hammett σ value for *para*-substituents Y in the tetrazole 5-aryl group (Figure). The product ratio was charge controlled and the reaction probably involved ambident attack by the tetrazolate anion at the carbon of the nitrile imide (**4**) (Scheme 1), since sufficient triethylamine was used to generate the tetrazolate anion as well as the nitrile imide. The substituent correlation noted (Figure) resembles a correlation which we previously observed[9] for alkylation of 5-aryltetrazolate anions by methyl iodide. There was no significant difference in the product ratios when the quantity of triethylamine was reduced to 1 mol equiv., but overall yields were lower and some benzoyl bromide hydrazone was recovered. No reaction occurred in the absence of triethylamine under the conditions used. *ortho*-Substituents in the 5-aryltetrazole did not sterically inhibit attack at the 1-N-position and indeed with 5-(*o,o*-dichlorophenyl)tetrazole hydrazone formation was slightly preferred at the 1-position. We previously observed[10] a similar preference for 1-*N*-attack in the methylation of 5-(*o,o*-dichlorophenyl)tetrazole and we believe it is due to a twisting of the plane of the phenyl and tetrazole rings allowing a weak complexation of the incoming electrophile with the orthogonal π-cloud of the aryl ring, thus giving an unexpected preferential attack at the 1-position (Structure **I**).



(**I**)

The substituents NH_2, $NHCH_2Ph$, and Me directly bonded at the tetrazole 5-carbon showed similar results and gave high yields of 1-hydrazonoyltetrazoles (Table 1); with H or Cl as the tetrazole 5-substituent, however, the hydrazonoyltetrazoles could not be isolated, *in situ* fragmentation to the 1,2,4-triazole products (**9m**) and (**11**) occurring instead (Scheme 2). Hydrazone formation for 5-amino- and 5-benzylamino-tetrazole was carried out at 0—5 °C in ethanol owing to the increased reactivity of the products which proceeded directly to triazoles at higher temperatures.

Fragmentative Cyclization of 1-Hydrazonoyltetrazoles to Substituted 1,2,4-*Triazoles.*—A hydrazone substituent on a heterocyclic ring is particularly interesting since it may provide an opportunity for a Boulton-Katritzky rearrangement,[11] a recent example[12] being the conversion of 1,2,4-oxadiazol-3-yl ketone hydrazones into 4-carbonylamino-1,2,3-triazoles, *e.g.* (**II**). With the 1-hydrazonoyltetrazoles (**2**) valency considera-

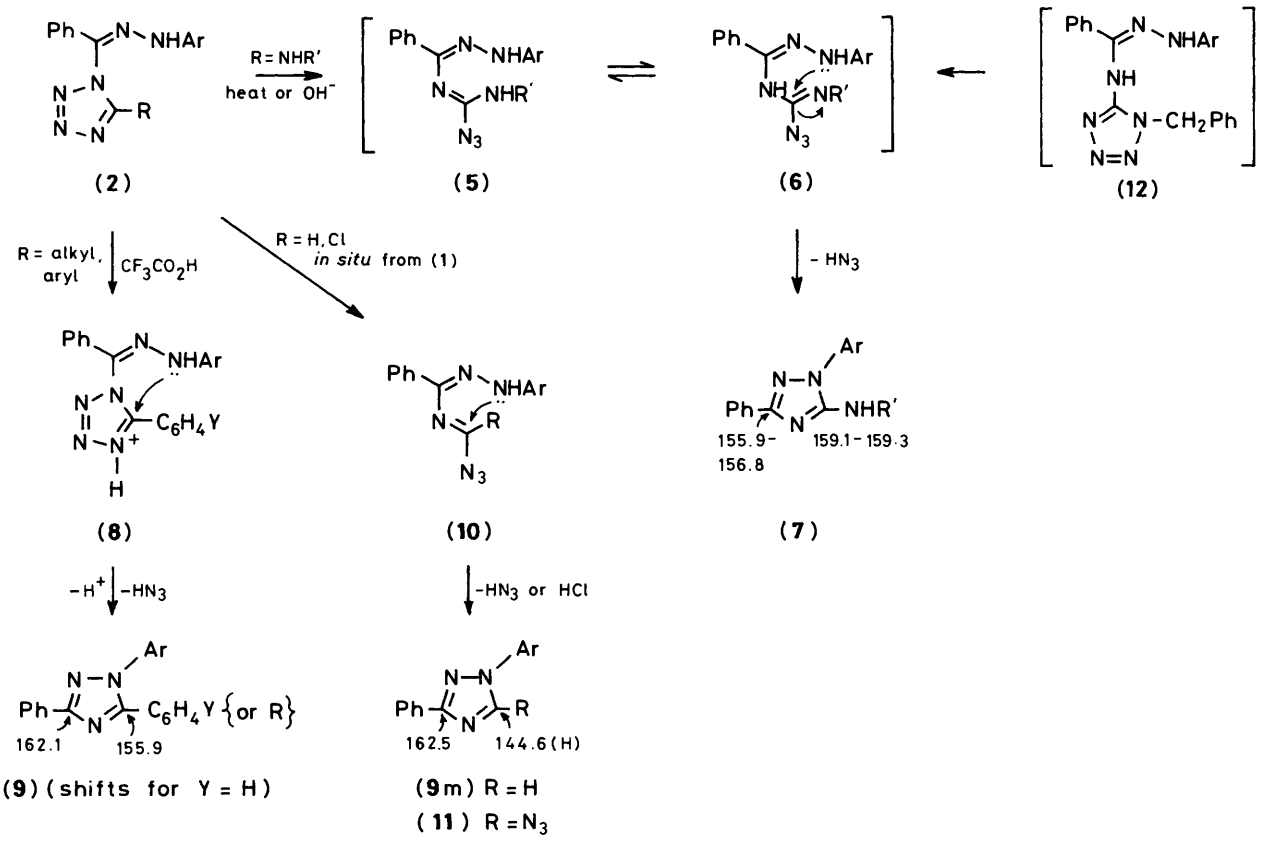


(**II**)

tions arising from bonding of the hydrazone group to the nitrogen of an N=C unit rather than the carbon atom would necessitate a modified Boulton-Katritzky process involving an elimination.

Direct isolation of the triazoles (**9m**) and (**11**) from the reactions of tetrazole and 5-chlorotetrazole with the nitrile imide suggested that such a useful fragmentative cyclization was occurring. It is likely that the electron withdrawing effect of the hydrazone group at the 1-position in compounds (**2**) destabilized the ring, as occurred with other deactivating groups such as CF_3 and SO_2R.[2,13] When the 5-substituent itself was further deactivating such as H and Cl this destabilization probably caused rapid ring opening to (**10**) which then cyclised with loss of HN_3 for R = H, and loss of HCl for R = Cl. The yield of the azide (**11**) (Table) was relatively low owing to competitive decomposition of 5-chlorotetrazole with Et_3N by elimination of HCl. Control reactions of $ClCN_4H$ with Et_3N under the conditions employed showed formation of Et_3N·HCl and resins comparable to those encountered in the reactions with 5-chlorotetrazole. When the tetrazole 5-substituent was an activating amino group compounds (**2**) (Scheme 2) were stable; however, on being heated under reflux in EtOH or briefly treated with ethanolic NaOH they readily underwent a fragmentative ring interconversion giving high yields of the triazoles (**7**) probably *via* the intermediates (**5**) and (**6**) (Scheme 2). Interestingly the product (**7**; R = $PhCH_2$) was also obtained in high yields when 5-amino-1-benzyltetrazole was treated with the nitrile imide in boiling ethanol. Intermediates of type (**2**) could not be involved in this reaction (5-amino-1-benzyltetrazole did not rearrange to 5-benzylaminotetrazole under the conditions) and the 5-NH_2 group probably added to the nitrile imide initially, giving the species (**12**), when the ring NH was blocked. Intermediates could not be isolated from these reactions even when carried out at 0 °C, but trace quantities of an unstable substance which changed to (**7**) on being dissolved in normal n.m.r. solvents and which showed an i.r. absorption at $\nu_{max.}$ 2 116 cm^{-1} were encountered as contaminants in the main product possibly indicating an azido intermediate such as (**5**) or (**6**) (Scheme 2).

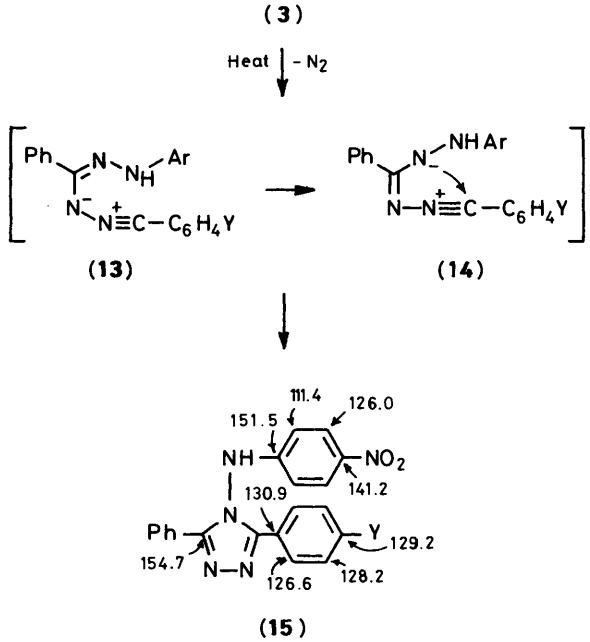
When the 5-tetrazole substituent R in compounds (**2**) (Scheme 2) was an alkyl or aryl group no reaction occurred on prolonged heating in boiling ethanol or on treatment with ethanolic NaOH and the compounds were remarkably unreactive. However, this difficulty was overcome by inducing a nucleophilic attack at the 5-carbon *via* protonation using trifluoroacetic acid. Thus treatment of the compounds (**2**) with trifluoroacetic acid readily gave high yields of the triazoles (**9**). Interesting



Scheme 2. Ar = p-$C_6H_4NO_2$ (some ^{13}C shifts in $CDCl_3$ shown)

substituent effects were observed for this reaction which we suggest occurs *via* protonation[14] at N-4 to give the species (**8**); this then undergoes nucleophilic attack at C-5 prior to, or simultaneous with, tetrazole ring opening (Scheme 2). In agreement with this, the qualitative order of reactivity for *para*-substituents in the tetrazole 5-aryl group was MeO > Me > H > Cl > NO_2 as determined from the yield of product and the quantity of compound (**2**) recovered for a series of reactions under identical standard conditions. Furthermore, the presence of two *ortho*-chloro substituents in the aryl ring totally inhibited the reactions and compound (**2**; R = *o*,*o*-dichlorophenyl) could not be converted into the corresponding compound (**9**) even though this reaction was readily achieved with a *para*-chloro or a single *ortho* chloro-substituent (Scheme 2). N.m.r. studies[10] have previously suggested an orthogonal twisting of the ring-planes [structure (**I**)] in 5-(*o*,*o*-disubstituted aryl)tetrazoles and such a geometry in the intermediate (**8**), which would be present prior to ring opening, would sterically block nucleophilic attack at C-5 by the hydrazone amino nitrogen from either side of the plane thereby inhibiting the triazole formation.

Thermolysis of 2-Hydrazonyltetrazoles.—Thermolysis of compounds (**3**) was also synthetically useful since they underwent a relatively clean, high-yield Huisgen reaction[2,3,7] giving the substituted 4-amino-1,2,4-triazoles (**15**) (Scheme 3) (Table, Part II). This reaction probably involved the intermediates (**7**) and (**14**) in a preferred 5-*endo*-digonal cyclization over the possible 6-*endo*-digonal alternative. This is the first example of *N*-amino-1,2,4-triazoles from the Huisgen reaction but the reaction has been used previously to synthesize other substituted 1,2,4-triazoles by treating tetrazoles with iminyl chlorides when the unstable 2-iminyltetrazole intermediates fragmented *in situ*.



Scheme 3. Full carbon-13 spectrum of compound (**15c**) shown

Thermolysis of 2,5-disubstituted tetrazoles is now a standard route to *C*,*N*-disubstituted nitrile imides.[1-3,15]

Product Structures.—The structures of the products were established by i.r. and ^1H and ^{13}C n.m.r. spectroscopy which

showed all the expected signals. All the compounds gave satisfactory C,H,N microanalyses.* The isomeric hydrazonyltetrazoles (**2**) and (**3**) were distinguished not only by their reactions (Schemes 2 and 3) but also by the tetrazole C-5 shift which, being highly sensitive[9,16] to the substituent pattern of the tetrazole ring, is 10—12 p.p.m. downfield in 2,5-disubstituted tetrazoles relative to 1,5-disubstituted isomers (where the signal usually appears at 154—156 p.p.m.) (Schemes 2 and 3).† The structures of the substituted 1,2,4-triazoles (**7**), (**9**), and (**11**) were also established from their i.r. and ^{1}H and ^{13}C n.m.r. spectra and were confirmed in a number of cases by unequivocal synthesis. Thus compound (**7**; R′ = H) (Scheme 2) was obtained by addition of cyanamide to benzonitrile *N*-(*p*-nitrophenyl)imide as well as from thermolysis of compound (**2j**). Direct benzylation of compound (**7**; R′ = H) with benzyl chloride and base gave the same product as that from thermolysis of compound (**2k**). As an example from the aryltetrazole series, the triazole (**9c**) was also prepared by direct addition of benzonitrile to the nitrile imide and found to be identical with the product from thermolysis of compound (**2c**) (Scheme 2). The structures of the triazoles (**15**) were also established from i.r. and ^{1}H and ^{13}C n.m.r. spectroscopy. Compound (**15c**) (Scheme 3) was particularly significant since it possesses a plane of symmetry and thus showed only the expected nine carbon signals thereby strongly supporting the assigned structure.

Experimental

M.p.s were measured on an Electrothermal apparatus. N.m.r. spectra were measured on JEOL JNM-GX-270, MH-100 and FX-60 instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvents. I.r. spectra were measured for mulls on a Perkin-Elmer 930G machine. The tetrazole substrates[1-3] and *N*-*p*-nitrophenylbenzohydrazonoyl bromide[17] were prepared by literature procedures. Each compound gave the expected ^{1}H and ^{13}C n.m.r. signals (Schemes). Proton spectra showed only expected aromatic signals and were less informative than the carbon spectra which generally showed each individual carbon with little overlap. Supplementary material (see earlier) contains full ^{13}C assignments for compounds (**2c**), (**2h**), (**2j**), (**2k**), (**2l**), (**3c**), (**3i**), (**7**; R′ = H), (**9c**), (**9h**), (**9l**), (**9m**), (**11**), (**15c**), (**15i**) and microanalytical data on all compounds. Carbon shift assignments were confirmed by off-resonance and selective proton decoupling and the aromatic carbon shifts showed the expected additivity for ring substituents.

Phenyl Tetrazolyl Ketone Hydrazones.—The following are typical examples. (*a*) A mixture of *N*-*p*-nitrophenylbenzohydrazonoyl bromide (m.p. 188—189 °C, lit.,[18] m.p. 190 °C) (640 mg, 2 mmol), 5-(*p*-tolyl)tetrazole (322 mg, 2 mmol), and benzene (20 ml) was stirred under reflux and treated dropwise with a solution of triethylamine (0.52 ml, 4 mmol) in benzene (10 ml) heated under reflux for 3 h. The mixture was then cooled, filtered to remove triethylammonium bromide, and evaporated. The residue (A) was leached with diethyl ether in a Soxhlet apparatus which extracted *phenyl* 5-(p-*tolyl*)*tetrazol*-2-*yl ketone* p-*nitrophenylhydrazone* (42%), m.p. 163—164 °C (from aqueous alcohol); $\nu_{max.}$ 3 283 (NH) and 1 590 cm^{-1} (C=N); δ_H[$(CD_3)_2SO$] 2.42 (s, *p*-Me) and 7.34—8.24 (m, Ar including two overlapping AA′BB′ systems). The ether-insoluble material was washed with cold water and dried to give *phenyl* 5-(p-*tolyl*)*tetrazol*-1-*yl ketone* p-*nitrophenylhydrazone* (**2b**) (50%), m.p. 146—148 °C (from ethanol); $\nu_{max.}$ 3 237 (NH) and 1 591 cm^{-1} (C=N); δ_H[$(CD_3)_2SO$] 2.43 (s, *p*-Me) and 7.32—8.32 (m, Ar with 2 AA′BB′). When a solution of the residue (A) in [$(CD_3)_2SO$] was analysed by ^{13}C n.m.r. spectroscopy the ratio of compound (**2b**) to (**3b**) was found to be 1.24:1 (Table, Part I).

(*b*) A mixture of *N*-*p*-nitrophenylbenzohydrazonoyl bromide (320 mg, 1 mmol), 5-aminotetrazole hydrate (103 mg, 1 mmol), and ethanol (10 ml) at 0—5 °C was stirred and carefully treated dropwise with a solution of triethylamine (0.26 ml, 2 mmol) in ethanol (5 ml) whereupon crystals of *phenyl* 5-*aminotetrazol*-1-*yl ketone* p-*nitrophenylhydrazone* (**2j**) separated and were collected after cooling (80%); m.p. 283—284 °C (from aqueous alcohol); $\nu_{max.}$ 3 443, 3 420, 3 345, and 3 193 (NH,NH_2) and 1 632 cm^{-1} (C=N); δ_H[$(CD_3)_2SO$] 7.21—8.24 (m, Ar). Work-up of the mother liquor gave further crude (**2j**) and starting material; the tetrazol-2-yl isomer was not encountered.

Similar reactions with tetrazole and 5-chlorotetrazole in either ethanol or benzene gave the triazoles (**9m**) and (**11**) respectively, hydrazonoyltetrazoles not being isolated.

Substituted 1,2,4-*Triazoles from* 5-*Substituted* 1-*Hydrazonoyltetrazoles.*—Typical examples are as follows. (*a*) A mixture of the hydrazone (**2b**) (200 mg), glacial acetic acid (10 ml), and trifluoroacetic acid (0.2 ml) was heated under reflux for 2 h. It was then evaporated to half-volume, diluted with water, and cooled to give crystals of 1-(p-*nitrophenyl*)-3-*phenyl*-5-(p-*tolyl*)-1,2,4-*triazole* (**9b**), m.p. 176—178 °C (from aqueous HOAc) (84%); $\nu_{max.}$ 1 608 cm^{-1}; δ_H($CDCl_3$) 2.40 (s, *p*-Me) and 7.21—8.26 (m, Ar). There was no reaction under neutral or basic conditions. These acidic conditions gave high yields (Table, Part II) of the triazoles (**9**) from the series (**2a**—**h**), the sole exception being compound (**2i**) which was recovered unchanged. Compound (**9c**) (68%) was also obtained when the hydrazonoyl bromide (740 mg), Et_3N (1.8 ml), and benzonitrile (20 ml) were heated at 100 °C for 7 h under nitrogen, the mixture evaporated, and the residue leached with benzene.

(*b*) The hydrazone (**2j**) (100 mg) in ethanol (20 ml) was heated under reflux for 3 h after which the mixture was evaporated to quarter volume and cooled to give crystals of 5-*amino*-1-(p-*nitrophenyl*)-3-*phenyl*-1,2,4-*triazole* (**7**; R′ = H) (95%), m.p. 292—294 °C (from aqueous ethanol); $\nu_{max.}$ 3 462, 3 419, 3 316, and 3 112 cm^{-1} (NH_2, with H-bonded tautomers) and 1 656 and 1 596 cm^{-1} (C=N); δ_H[$(CD_3)_2SO$] 7.09 (br, NH) and 7.53—8.49 (Ar, including AA′BB′). In the presence of NaOH (1 mol) the reaction was complete in 10 min; it is also possible to transform 5-aminotetrazole to compound (**7**; R′ = H) *in situ* by heating the reaction solution without isolation of the hydrazonoyltetrazole. The product (**7**; R′ = H) (20%) was also obtained when the hydrazonoyl bromide (320 mg) and cyanamide (126 mg) in ethanol (10 ml) was stirred under reflux with triethylamine (0.13 ml) and ethanol (5 ml). Separation of the products on a silica gel column using ethyl acetate–light petroleum (b.p. 60—80 °C) (3:1, v/v) as eluant gave the known[18] hydrazonoyl ether PhC(OEt)=NNHAr, m.p. 166—168 °C (lit.,[18] m.p. 168 °C). Compound (**7**; R′ = H) (100 mg) in ethanol (15 ml) was heated and treated with 10% NaOH (0.128 ml) and then benzyl chloride (0.04 ml). After being heated under reflux for 5 h, the mixture was worked up by column chromatography as described above to give 5-*benzylamino*-1-(p-*nitrophenyl*)-3-*phenyltriazole* (**7**; R′ = $PhCH_2$) (12%) (m.p. 159—160 °C together with starting material (87%); $\nu_{max.}$ 3 419 (NH) and 1 609 cm^{-1} (CN); δ_H[$(CD_3)_2SO$] 4.70 (d, CH_2NH) and 7.24—8.29 (m, Ar). This sample of compound (**7**; R′ = $PhCH_2$) was identical with that obtained (87%) from thermolysis of

* These results have been treated as a Supplementary publication SUP. No. 56712 (10 pp.)]. See Instructions for Authors (1988), *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1, for details of the Scheme.

† The 5-C shift ranges in Schemes 2 and 3 do not include the 5-(*o*,*o*-dichlorophenyl) derivatives whose shifts were outside the normal ranges due to the ring rotations and were 150.4 in structure (**2**) and 159.9 p.p.m. in structure (**3**).

compound (**2k**) and from the reaction of the nitrile imide with 5-amino 1-benzyltetrazole (70%).

Substituted 1,2,4-*Triazoles* (**15**) *from* 5-*Substituted* 2-*Hydrazonoyltetrazoles*.—Typically, a mixture of compound (**3b**) (150 mg) in hexanol (10 ml) was stirred and heated under reflux for 5 h; the mixture was then evaporated to quarter volume and crystallisation induced with a glass rod to give 4-(p-*nitroanilino*)-3-*phenyl*-5-(p-*tolyl*)-1,2,4-*triazole* (**15b**) (89%), m.p. 252—253 °C (from hexanol); $\nu_{max.}$ 3 177 and 3 134 (NH) and 1 596 cm^{-1} (CN); δ_H 5.30 (br, NH), 6.60 (d), 7.02 (d), 7.21—7.35 (m), 7.64 (d), 7.75 (d), 8.00 (d, 15 H with two AA'BB' systems, Ar).

Acknowledgements

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