N-Amination and Subsequent Oxidation of Some Fused Imidazoles and Triazoles

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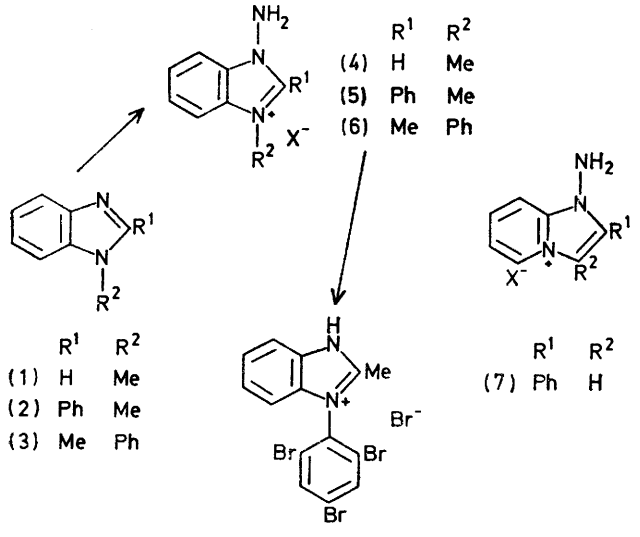
N-Amination of imidazo[1,2-*a*]pyridines, pyrido[1,2-*a*]benzimidazole, *s*-triazolo[1,5-*a*]pyridines, and *s*-triazolo[4,3-*a*]pyridines is described. 1-Amino-*s*-triazolo[1,5-*a*]pyridinium salts were also obtained by cyclizing 2-(2-acylhydrazino)-1-aminopyridinium salts. Oxidation of 10-aminopyrido[1,2-*a*]benzimidazolium bromide and 1-amino-*s*-triazolo[1,5-*a*]pyridinium salts with bromine gave 10,10'-azopyrido[1,2-*a*]benzimidazolium and 1,1'-azo-*s*-triazolo[1,5-*a*]pyridinium salts, respectively. Similar oxidation of 3-amino-2-methyl-1-phenylbenzimidazolium bromide and 1-amino-*s*-triazolo[4,3-*a*]pyridinium salts resulted in deamination.

1-AMINO-3-METHYLBENZIMIDAZOLIUM salts and 1-aminoimidazo[1,2-*a*]pyridinium salts of the types (5) and (7), respectively, are the precursors for the preparation of



	R^1	R^2
(1)	H	Me
(2)	Ph	Me
(3)	Me	Ph

	R^1	R^2
(4)	H	Me
(5)	Ph	Me
(6)	Me	Ph

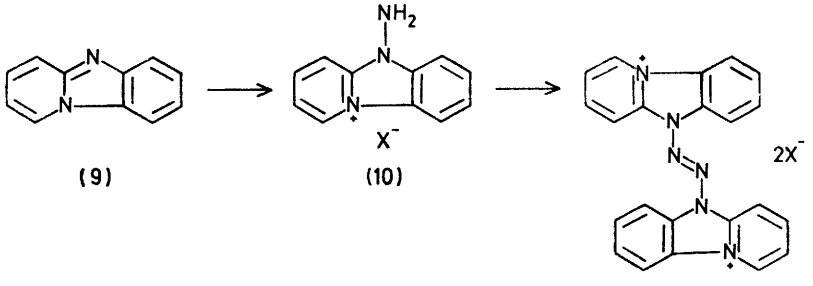
	R^1	R^2
(7)	Ph	H

(8)

the corresponding 3,3'-dimethyl-1,1'-azobenzimidazolium salts [1] and 1,1'-azoimidazo[1,2-*a*]pyridinium salts,[2] which possess useful neuromuscular blocking activity of the non-depolarising type. The *N*-amino-salts (5) and (7) are, however, derived from *o*-nitrophenylhydrazine and 1-acetyl-2-pyridylhydrazine,[2] respectively, both of which are relatively expensive. The direct *N*-amination of *N*-methylbenzimidazoles and imidazo[1,2-*a*]pyridines was therefore investigated as a cheaper route to *N*-amino-salts of the types (5) and (7).

The *N*-amination of imidazo[1,2-*a*]pyridine in low yield by hydroxylamine-*O*-sulphonic acid has been reported previously,[2] but attempts to prepare the phenyl compound (7) similarly failed, as did attempts [3,4] to *N*-aminate *N*-methylbenzimidazole and *N*-methylimidazole. By use of the recently described powerful *N*-aminating agent *O*-mesitylsulphonylhydroxylamine [5] (MSH), however, the *N*-substituted benzimidazoles (1) and (2) were *N*-aminated in good yield, but the relatively high cost of mesitylenesulphonyl chloride, from which the *N*-aminating agent was derived, still rendered the procedure unattractive. Consequently the use of the analogous reagent *O*-*p*-tolylsulphonylhydroxylamine (TSH), derived from the cheap and readily available toluene-*p*-sulphonyl chloride, was contemplated.

TSH (13) was obtained by hydrolysis of ethyl O-*p*-tolylsulphonylacetohydroximate (12), which in turn was prepared by treating ethyl acetohydroximate [6] with toluene-*p*-sulphonyl chloride in the presence of base. The TSH was too unstable for recrystallization and attempts to dry it led to vigorous decomposition.[7] The reagent was best extracted into chloroform; after drying with sodium sulphate the solution could be stored for a short time, but it slowly deposited ammonium toluene-*p*-sulphonate. Surprisingly, when the solution was boiled under reflux and the precipitated ammonium toluene-*p*-sulphonate filtered off, evaporation of the filtrate gave



(9) (10) (11)

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[2] E. E. Glover and M. Yorke, *J. Chem. Soc.* (*C*), 1971, 3280.
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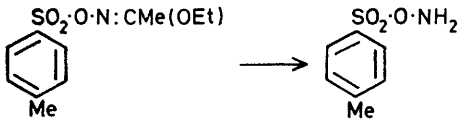
the acetone condensation product (15). Thus 2-phenylimidazo[1,2-*a*]pyridine,[8] pyrido[1,2-*a*]benzimidazole (9),[9] and the methylbenzimidazoles (1)—(3) were successfully *N*-aminated (Table 1).



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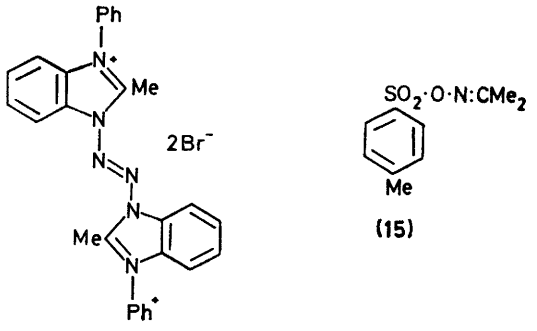


(14) (15)

Oxidation of the tricyclic *N*-amino-salt (10) with bromine gave the expected diquaternary tetrazene (11), but similar oxidation of 3-amino-2-methyl-1-phenylbenzimidazolium bromide (6) gave the brominated hydrobromide (8) instead of the expected diquaternary tetrazene (14).

Although 1,1′-azoimidazopyridinium salts [2] (16) have useful neuromuscular blocking properties of the non-depolarising type,[10] their duration of action in man is longer than that required of an ideal muscle relaxant.[11] These properties are also shown by 1,1′-azobenzimidazolium salts [1] (17), which in addition exhibit increased brevity of action; unfortunately, however, the chemical stability of the latter compounds in solution is correspondingly less.[4] The possibility of combining the desirable shorter acting property of the benzimidazolium salts (17) with the greater chemical stability of the imidazopyridinium salts (16) was therefore considered, and the synthesis of the 1,1′-azo-*s*-triazolopyridinium salts (18)—(20) undertaken. The proposed route proceeded *via* oxidation with bromine of the 1-aminotriazolopyridinium salts (24)—(26) obtained either by direct *N*-amination of the corresponding triazolopyridines (21)—(23) or by cyclization of the 2-(2-acylhydrazino)-1-aminopyridinium salts (29) and (30).

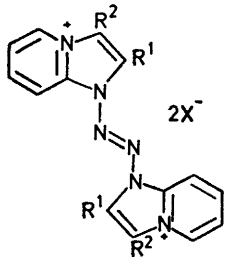
The conversion of 2-aminopyridine into 1,2-diaminopyridinium salts with hydroxylamine-*O*-sulphonic acid has been reported previously,[12] but the reaction proceeds in better yield with MSH. This reagent also effected *N*-amination of 1-benzoyl-2-(2-pyridyl)hydrazine (28), yielding (30) in high yield; boiling hydrobromic acid then converted (30) into the bicyclic *N*-amino-salt (26), presumably *via* an acyl group migration akin to that occurring in the formation of 1-aminobenzimidazoles from 1-acyl-2-(*o*-aminophenyl)hydrazines.[1,13] The same bicyclic *N*-amino-compound (26) was obtained by *N*-amination of the 2-phenyltriazolopyridine (23) with MSH.

Treatment of 1-acetyl-2-(2-pyridyl)hydrazine [2] (27) with MSH gave the corresponding 1-aminopyridinium salt (29), which underwent thermal cyclization to the methyl *N*-amino-compound (25).

Attempted formylation of 2-pyridylhydrazine with boiling formic acid gave the parent triazolo[4,3-*a*]-pyridine (31), which was converted into the *N*-amino-salt (35) with TSH.

Oxidation of the bicyclic *N*-amino-salts (24)—(26) with saturated aqueous bromine gave the required azotriazolopyridinium salts (18)—(20), the u.v. spectra of which showed characteristic long-wave maxima in the 350 nm region.

It has been reported [14] that quaternization of methyl-



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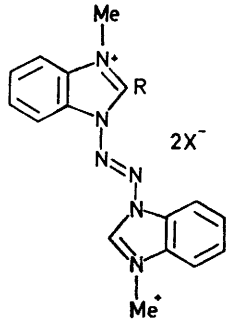

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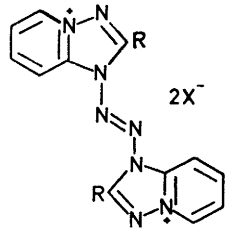

R

(18) H
(19) Me
(20) Ph

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TABLE 1

N-Amino-salts

Reactants	Product No	Product X	Yield (%)	M.p. (°C)	Cryst. solvent	Found (%) C	Found (%) H	Found (%) N	Rqd. (%) C	Rqd. (%) H	Rqd. (%) N
(1) (0.4 g) + MSH [a] (0.6 g) in CH_2Cl_2 (15 ml) [b]	(4)	$C_9H_{11}SO_3$ *	66	229	EtOH	58.8	6.2	11.9	58.8	6.1	12.1
	(4)	Br [c]		262 [d]	EtOH						
(2) [e] (0.1 g) + MSH [a] (0.1 g) in CH_2Cl_2 (10 ml) [b]	(5)	$C_9H_{11}SO_3$ *	74	230	MeOH–Et_2O	65.3	6.1	9.9	65.2	5.95	9.9
	(5)	Br [c]		255 [f]	EtOH–Et_2O						
(3) [15] (2.3 g) + 5% w/w solution of TSH [g] in $CHCl_3$ (52 ml) [h]	(6)	Br	53	118	EtOH–Et_2O	52.1	5.1	13.3	52.2	5.0	13.0 [i]
(9) [9] (1.2 g) + TSH [g] (1.7 g) in CH_2Cl_2 (20 ml) [b]	(10)	$C_7H_7SO_3$ ‡	87	195—196	MeOH–Et_2O	60.8	4.5	11.8	60.8	4.8	11.8
	(10)	Br [c]		248	Pr^nOH–Petroleum (b.p. 60—80°)	49.9	4.0	15.4	50.0	3.8	15.9
2-Phenylimidazo[1,2-*a*] pyridine [8] (2.0 g) + 5% solution of TSH [g] in $CHCl_3$ (50 ml) [j]	(7)	$C_7H_7SO_3$ ‡	24	181—182	MeOH–Et_2O	62.9	5.1	10.9	63.0	5.0	11.0
	(7)	Br		191—192 [k]	EtOH–Et_2O	53.7	4.4	14.5	53.8	4.2	14.5
2-Aminopyridine (0.47 g) in CH_2Cl_2 (15 ml) + TSH [g] (0.95 g) [b]		$1,2\text{-}(NH_2)_2C_5H_4\overset{+}{N}$ $C_7H_7SO_3^-$	80	164—165	MeOH–Et_2O	51.5	5.4	14.9	51.2	5.4	14.9
2-Aminopyridine (0.3 g) in CH_2Cl_2 (10 ml) + MSH [a] (0.69 g) [b,l]		$1,2\text{-}(NH_2)_2C_5H_4\overset{+}{N}$ $C_9H_{11}SO_3^-$	52	135—136	EtOH–Et_2O	54.6	6.2	13.5	54.4	6.2	13.6
(28) [16] (0.947 g) in CH_2Cl_2 (20 ml) + MSH [a] (0.947 g) [m]	(30)	Br	57	229—230	MeOH–Et_2O	46.2	4.6	18.3	46.6	4.2	18.1
(23) [12] (0.4 g) in CH_2Cl_2 (10 ml) + MSH [a] (0.441 g) [n]	(26)	$C_9H_{11}SO_3$ *	17	189—190	MeOH–Et_2O	61.5	5.7	13.5	61.5	5.4	13.7
(30) (0.78 g) in 24% HBr (15 ml) [o]	(26)	Br	79	232—233	EtOH–Et_2O	49.2	4.2	19.1	49.5	3.8	19.2
(27) [2] (0.7 g) in CH_2Cl_2 (30 ml) + MSH [a] (1.0 g) [p]	(25)	$C_9H_{11}SO_3$ *	62	236—237	MeOH–Et_2O	54.9	5.9	15.75	55.2	5.8	16.1
	(25)	Br [c]		232	EtOH	36.7	3.9	24.7	36.7	4.0	24.5
(21) [12] (0.41 g) in CH_2Cl_2 (15 ml) + TSH [g] (0.65 g) [b]	(24)	$C_7H_7SO_3$	54	228—229	MeOH–Et_2O	50.9	4.9	18.3	51.0	4.6	18.3
	(24)	Br [c]		260 [q]	MeOH–Et_2O	33.5	3.4	25.8	33.5	3.3	26.05
(31) [e] (2.2 g) in CH_2Cl_2 (40 ml) + TSH [g] (3.3 g) [n]	(35)	$C_7H_7SO_3$ ‡	52	204—206	MeOH–Et_2O	51.1	4.5	18.2	51.0	4.6	18.3
	(35)	Br [r]		170	MeOH–Et_2O	33.2	3.5	25.55	33.5	3.3	26.05
(32) [u] (2.45 g) in CH_2Cl_2 (45 ml) + TSH [g] (3.5 g) [n]	(36)	$C_7H_7SO_3$‡	56	263—265	MeOH–Et_2O	52.3	49.5	17.7	52.5	5.0	17.5
	(36)	Br [o]		270—272 [j]	MeOH–Et_2O	36.9	3.8	24.8	36.7	4.0	24.5
(33) [17] (0.165 g) in CH_2Cl_2 (7.5 ml) + MSH [a] (0.18 g) [n]	(37)	$C_9H_{11}SO_3$ *	52	207—209	EtOH–Et_2O	60.5	5.6	14.0	60.1	5.5	13.4 [t]
	(37)	Br [r]		234—235	MeOH–Et_2O	49.1	4.3	19.2	49.5	3.8	19.2

[a] *O*-Mesitylsulphonylhydroxylamine. [b] The *N*-aminating agent was added in small portions to the stirred solution of the base and the stirring was continued for a further 0.25 h. Ether was then added and the precipitated salt filtered off and recrystallized. [c] Prepared by treating a concentrated solution of the mesitylenesulphonate or toluene-*p*-sulphonate salt in ethanol with 48% hydrobromic acid–ether. [d] Lit.,[1] m.p. 262°. [e] Prepared by boiling under reflux for 3.5 h a solution of 1-amino-2-methylaminobenzene (12 g) and benzoyl chloride (1.38 g) in pyridine (15 ml). The solution was then evaporated under reduced pressure and the residue treated with water, and extracted with chloroform. Evaporation of the dried extract and vacuum distillation of the residue gave an oil which solidified on trituration (1.5 g, 73%). The base crystallized from ether–petroleum (b.p. 40—60°) as prisms, m.p. 98° (lit.,[18] 98°) (Found: C, 80.8; H, 6.0; N, 13.3. Calc. for $C_{14}H_{12}N_2$: C, 80.7; H, 5.8; N, 13.45%). [f] Lit.,[1] m.p. 255°. [g] *O*-*p*-Tolylsulphonylhydroxylamine. [h] The solution was stirred for 0.5 h and then evaporated to dryness under reduced pressure. The residue was dissolved in the minimum volume of alcohol and the solution treated with 48% hydrobromic acid–ether, giving the bromide, which was filtered off and recrystallized. [i] For $1H_2O$. [j] The solution was stirred for 0.5 h and ether was added. The precipitated solid was then filtered off and recrystallized. [k] Lit.,[2] m.p. 177—179° (monohydrate). [l] The product precipitated as an oil but solidified on trituration with ether. [m] The MSH was added to the stirred solution in small portions over 5 min. Stirring was continued for 0.25 h after the solution had cleared and then the solution was evaporated.,The residue was dissolved in ethanol and treated with 48% HBr followed by ether. The precipitated bromide was then filtered off and recrystallized. [n] The *N*-aminating agent was added to the stirred solution in small portions and the stirring continued for a further 0.5 h. Ether was then added and the precipitated salt filtered off and recrystallized. [o] The solution was boiled under reflux for 1 h and then evaporated to dryness, and the residue was recrystallized. [p] As in *n* but the hygroscopic product was then heated at 160—170 °C for 3 h before recrystallization. [q] With decomp. [r] Prepared by stirring for 24 h a suspension of Amberlite IRA 400 resin (Br^-) in an aqueous solution of the toluene-*p*- or mesitylene-sulphonate salt. [s] Obtained by the procedure described in ref. 19. The *picrate* crystallized from nitromethane as yellow prisms, m.p. 249° (Found: C, 41.6; H, 2.2; N, 24.45. $C_6H_5N_3,C_6H_3N_3O_7$ requires C, 41.4; H, 2.3; N, 24.1%). [t] For the hemihydrate. [u] Prepared by boiling a solution of 1-acetyl-2-(2-pyridyl)hydrazine (3.0 g) in glacial acetic acid (25 ml) for 4 h. The solution was then evaporated under reduced pressure, the residue basified and extracted with chloroform, and the dried chloroform extract evaporated. Evaporation of the residue onto a cold finger followed by resublimation gave the base (2.43 g, 92%), m.p. 133° (lit.,[19] 134°) (Found: C, 62.6; H, 5.5, N.31.8. Calc. for $C_7H_7N_3$: C, 63.1; H, 5.3; N, 31.6%).

* Mesitylenesulphonate salt. ‡ Toluene-*p*-sulphonate salt.

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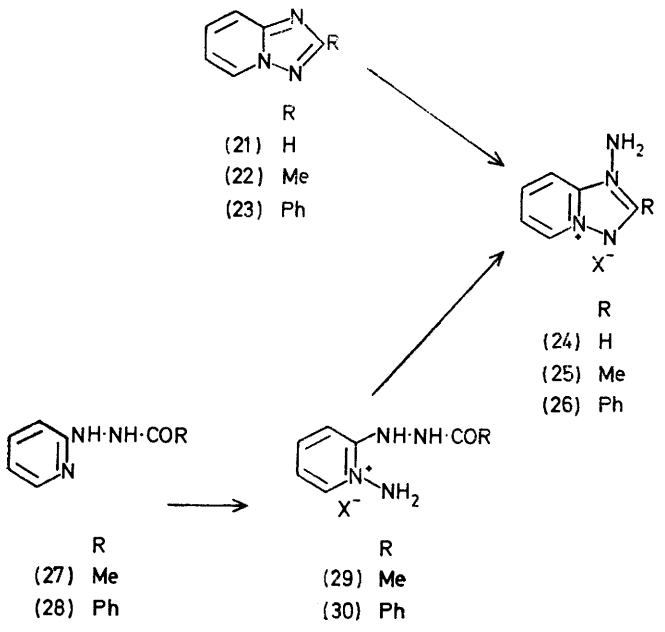
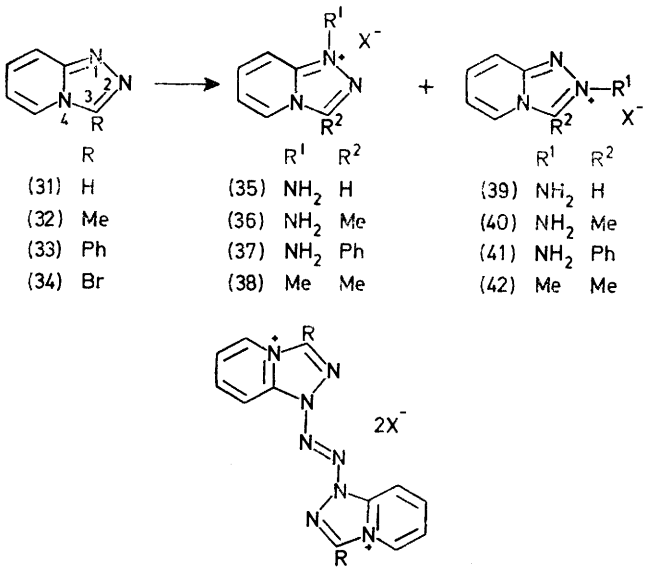
triazolo[4,3-*a*]pyridin-3-yl sulphide and 3-amino-triazolo-[4,3-*a*]pyridine with methyl iodide occurs at N-1 and N-2,



respectively. We have found that similar quaternization of the 3-methyl compound (32) gives a mixture of 1,3-(38) (65%) and 2,3-dimethyltriazolopyridinium iodide (42) (35%), the composition of the mixture being determined from its ^{1}H n.m.r. spectrum on the assumption that the 3-Me signal of (42), in which quaternization has occurred on the adjacent N-2, occurs downfield of that of (38), in which quaternization has occurred at N-1. Similarly, quaternization of 3-methyl-*s*-triazolo[4,3-*a*]-pyridine (32) with TSH was shown to give a mixture of the 1-amino-3-methyl-*s*-triazolo[4,3-*a*]pyridinium salt (36) (87%) and the corresponding 2-amino-compound (40)



(13%). It was concluded, therefore, that *N*-amination of the parent base (31) and the phenyl compound (33)

TABLE 2

Oxidation of *N*-amino-salts

Starting *N*-amino-bromide	Vol of sat. aq. Br_2(ml)	Product No.	Product X	Yield (%)	M.p. (°C)	Crystallizing solvent	Found (%) C	Found (%) H	Found (%) N	Rqd. (%) C	Rqd. (%) H	Rqd. (%) N
(10) (0.4 g) [a]	60	(11)	Br [b]	65	254—255	48% HBr–Me_2CO	47.8	3.15	14.8	47.9	3.5	15.2 [c]
		(11)	$C_6H_2N_3O_7$ [d]		231	$MeNO_2$	50.2	2.2	20.4	49.8	2.5	20.5
(6) (0.2 g) [a]	40	(8)	Br [e]	35	256	MeOH–Et_2O	32.1	1.7	5.4	32.0	1.9	5.3
(24) (0.2 g) [f,g]	30	(18)	Br [h]	53	302 [i]	48% HBr–Me_2CO	33.1	2.6	25.5	33.1	2.55	25.75 [j]
		(18)	$C_6H_2N_3O_7$ [d]		189	$MeNO_2$	39.3	2.0	27.2	39.9	1.95	27.15
(25) (0.11 g) [k]	11	(19)	Br [l]	54	302 [i]	MeOH–Et_2O	34.3	3.8	22.9	34.3	3.7	22.9 [m]
		(19)	$C_6H_2N_3O_7$ [d]		246—248	$MeNO_2$	41.4	2.5	26.5	41.6	2.4	26.1
(26) (0.1 g) [f]	15	(20)	Br [n]	28	254 [i]	MeOH–Et_2O	47.2	3.9	18.2	46.9	3.6	18.2 [m]
		(20)	$C_6H_2N_3O_7$ [d]		245	$MeNO_2$	49.2	2.65	22.45	49.4	2.5	22.4
(35) (0.5 g)	80 [o]	(34) [p]		26	165—167 [q]		36.0	2.2	20.95	36.4	2.0	21.2
(36) (0.5 g) [a,g]	100	(32) [p]		28	133 [r]		62.6	5.5	31.8	63.1	5.3	31.6
(37) (0.1 g) [s]	20 [t]	(33)	Hydrobomide salt	58	237—239	MeOH–Et_2O	52.1	3.45	15.3	52.2	3.65	15.2

[a] A saturated solution of the bromide was treated in bulk with the saturated aqueous bromine and the solution was agitated until the precipitate coagulated. This was then filtered off and boiled with absolute acetone giving the product, which was filtered off and recrystallized. [b] $\lambda_{max.}$(H_2O) 204, 233, 293, 327sh, 373sh, and 391nm ($\log_{10}\varepsilon$ 4.73, 4.73, 4.23, 3.88, 4.62, and 4.70). [c] For $1.5H_2O$. [d] Picrate. [e] Identical with a sample obtained by stirring a solution of the base (3) in methanol with saturated aqueous bromine for 1 h followed by evaporation to dryness and treatment of the residue with ethanol followed by 48% hydrobromic acid–ether. [f] A saturated aqueous solution of the bromide at 60 °C was treated in bulk with the saturated aqueous bromine and the solution was kept at 60 °C for a further 5 min. The solution was then cooled and the precipitated red perbromide separated and boiled with absolute acetone giving the yellow tetrazene dibromide. [g] The precipitated perbromide was a red oil. [h] $\lambda_{max.}$(H_2O) 200 and 342 nm ($\log_{10}\varepsilon$ 4.65 and 4.24). [i] With decomp. [j] For the hemihydrate. [k] A saturated aqueous solution of the bromide at 50 °C was treated in bulk with the saturated aqueous bromine and the solution was cooled. The precipitated red perbromide was then filtered off and boiled with absolute acetone, giving the yellow tetrazene dibromide. [l] $\lambda_{max.}$(H_2O) 198 and 348 nm ($\log_{10}\varepsilon$ 4.74 and 4.46). [m] For $2H_2O$. [n] $\lambda_{max.}$(H_2O) 201, 238, 250sh, 252sh, 262sh, 264sh, 269sh, 279sh, and 351 nm ($\log_{10}\varepsilon$ 4.84, 4.46, 4.39, 4.36, 4.24, 4.14, 3.95, and 4.38). [o] The bromine was added in bulk to a concentrated aqueous solution of the *N*-amino-bromide and the solution was then heated on a boiling water-bath for 4 h. The solution was then evaporated and the residue boiled with acetone. The resulting buff solid was filtered off, dissolved in water, and basified, and the solution was then continuously extracted with chloroform (8 h). Evaporation of the extract gave the product, which was evaporated under reduced pressure onto a cold finger. [p] Purified by vacuum sublimation. [q] Lit.,[12] m.p. 165 °C. [r] Lit.,[19] m.p. 134 °C. [s] A saturated methanolic solution of the bromide was treated in bulk with the bromine solution and the whole was then heated on a water-bath at 80 °C for 0.25 h. The solution was then evaporated and the residue recrystallized. [t] Saturated solution in 50% aqueous methanol.

occurred mainly at N-1, giving the *N*-amino-quaternary salts (35) and (37), respectively.

Oxidation of the 1-aminotriazolo[4,3-*a*]pyridinium salts (36) and (37) with bromine failed to give the corresponding tetrazenes (43), the only products isolated being the parent bases (32) and (33), respectively. Similar oxidation of the unsubstituted *N*-amino-salt (35) likewise resulted in deamination, but in this case the only product isolated was the brominated base (34).

EXPERIMENTAL

M.p.s. were determined with a Kofler hot-stage apparatus. U.v. and ^{1}H n.m.r. spectra were determined with Perkin-Elmer 237 and R12A spectrometers, respectively.

Ethyl O-p-*Tolylsulphonylacetohydroximate* (12).—An ice-cold solution of freshly prepared ethyl acetohydroximate [6] (4.5 g) and triethylamine (4.5 g) in dimethylformamide (30 ml) was treated with toluene-*p*-sulphonyl chloride (8.3 g) over 10 min and the solution was stirred for a further 2 h at room temperature. The triethylamine hydrochloride which had separated was then filtered off and washed with ether. Evaporation of the ether from the combined filtrate and washings followed by addition of the residual solution to ice-cold water (300 ml) gave the hydroximate (7.0 g, 62%), which crystallized from aqueous methanol as prisms, m.p. 70—71° (Found: C, 51.3; H, 5.7; N, 5.7. $C_{11}H_{15}NO_4S$ requires C, 51.4; H, 5.9; N, 5.4%).

O-p-*Tolylsulphonylhydroxylamine* (13).—A suspension of the hydroximate (12) (2.0 g) in 60% perchloric acid (15 ml) was stirred at room temperature; the hydroximate dissolved and a solid separated. The suspension was poured onto crushed ice and the mixture extracted with methylene chloride. Evaporation of the dried (Na_2SO_4) extract gave the hydroxylamine (1.1 g, 75.6%), m.p. 40 °C (capillary). The product was too unstable for recrystallization but could be stored for about 1 week in solution in chloroform, from which ammonium toluene-*p*-sulphonate was slowly deposited; it had m.p. 263—265° (from MeOH—Et_2O) (Found: C, 44.45; H, 5.8; N, 7.6. $C_7H_{11}NO_3S$ requires C, 44.5; H, 5.9; N, 7.4%).

Acetone *O*-*p*-tolylsulphonyloxime (15) crystallized from ethanol as plates, m.p. 86° (lit.,[7] 86—88°) (Found: C, 52.5; H, 5.9; N, 6.0. Calc. for $C_{10}H_{13}NO_3S$: C, 52.9; H, 5.8; N, 6.2%).

We thank Allen and Hanburys Research Ltd. for a fellowship (to K. T. R.).

[5/1225 *Received*, 23*rd June*, 1975]