1,2,3-Triazoles produced from 5-Substituted *N*-Methoxytriazolium Salts

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Five reactions, two of which are new, have been observed when 5-substituted 1-methoxy-2-phenyltriazolium salts react with nucleophiles: (i) addition to C-4 with elimination of methanol to give unsymmetrically 4,5-disubstituted triazoles; (ii) displacement of the 5-substituent followed by secondary reactions to give a symmetrically 4,5-disubstituted triazole, a 5-substituted triazole *N*-oxide, a 4-substituted triazole, or a disubstituted benzeneazoacetonitrile; (iii) deprotonation of the *N*-methoxy-group with elimination of formaldehyde; (iv) demethylation; (v) abstraction of an α-proton from a 5-alkyl group followed by nucleophilic addition and elimination of methanol to give an α-substituted 5-alkyltriazole. The reactions are of synthetic potential as a means of introducing one or two substituents in the 1,2,3-triazole system.

The low reactivity of the heteroaromatic nucleus of 2-phenyl-1,2,3-triazoles towards electrophiles and nucleophiles is enhanced by an *N*-oxide function, as in compound (1); this activates the adjacent ring position so that hydrogen can be replaced by neutral electrophiles, and halogen by strong nucleophiles.[1] Further activation is attained by alkylation of the *N*-oxygen atom; thus methoxy-compound (2; X = H) undergoes addition with weak nucleophiles. Subsequent elimination of methanol affords a substituted triazole (9). In this way a series of triazoles (9), monosubstituted with halogen, oxygen, nitrogen, sulphur, and carbon, has been obtained.[1] 1-Methoxytriazolium salts (2), which have substituents at the carbon atom adjacent to the *N*-methoxy-group, give adducts (5); these are unable to expel methanol by 1,2-elimination. In such cases, the reaction takes other courses which have now been investigated in order to reveal their mechanism and synthetic potential. Again,[1] the triazoles may serve as models for other five-membered nitrogen heteroaromatics.

5-Substituted 1-methoxytriazolium salts (2) are obtained in high yield by alkylation of 5-substituted triazole *N*-oxides (1) (Scheme 1), which in their turn are accessible by the replacement reactions of simpler triazole *N*-oxides or by ring closure of suitable precursors.[1] Thus, 5-chloro-1-methoxytriazolium tetrafluoroborate (2a) was prepared *via* chlorination of the triazole *N*-oxide (1; X = H) followed by methylation with trimethyloxonium tetrafluoroborate. The 1-methoxy-5-methylthiotriazolium salt (2b) was obtained similarly from methylthiotriazole *N*-oxide (1b) which was prepared by treatment of chlorotriazole *N*-oxide (1a) with methanethiolate ions. The 1-methoxy-5-methyltriazolium salt (2c) was synthesized from 2-hydroxyiminopropanal by treatment with phenylhydrazine followed by oxidative cyclization to give the 5-methyltriazole *N*-oxide (1c); this was *O*-alkylated to give the methoxy-derivative (2c).

The 5-chloro, 5-methylthio-, and 5-methyl-1-methoxytriazolium salts (2a—c) represent 1-methoxytriazolium ions substituted with a good leaving group, a poor leaving group, and a group incapable of acting as a leaving group, respectively. At least five principal routes (i—v) can be envisaged for the reactions of (2a—d) with nucleophiles.

Of these, (iii) and (iv) are known from 1-methoxypyridinium salts [2] and have also been observed in 5-unsubstituted 1-methoxytriazolium salts.[1] Neither (iii) nor (iv) are of preparative interest in the present context. Reaction mode (iv), *O*-dealkylation, leads to regeneration of the triazole *N*-oxide (1). Reaction mode (iii) involves deprotonation of the *O*-methyl group followed by elimination of formaldehyde to give the 4-substituted triazole (9). These are more easily accessible through deoxygenation of 5-substituted triazole *N*-oxides (1) [1] or by nucleophilic addition to 1-methoxytriazolium salts (2; X = H) which are devoid of substituents at C-5.

Reaction path (i) has apparently not been observed in other *N*-methoxy-substituted heteroaromatics. It implies nucleophilic addition to the ring carbon β to the *N*-methoxy-group of the salt (2) with simultaneous loss of methoxide. Subsequent aromatization through loss of 4-H leads to a 4,5-disubstituted triazole (4), with two different substituents if desired. Only a few such triazoles are known, and these are mainly derivatives of 4-carboxy-5-hydroxy- and 4-amino-5-carboxy-triazoles.[3] Therefore, reaction mode (i) is of considerable synthetic potential.

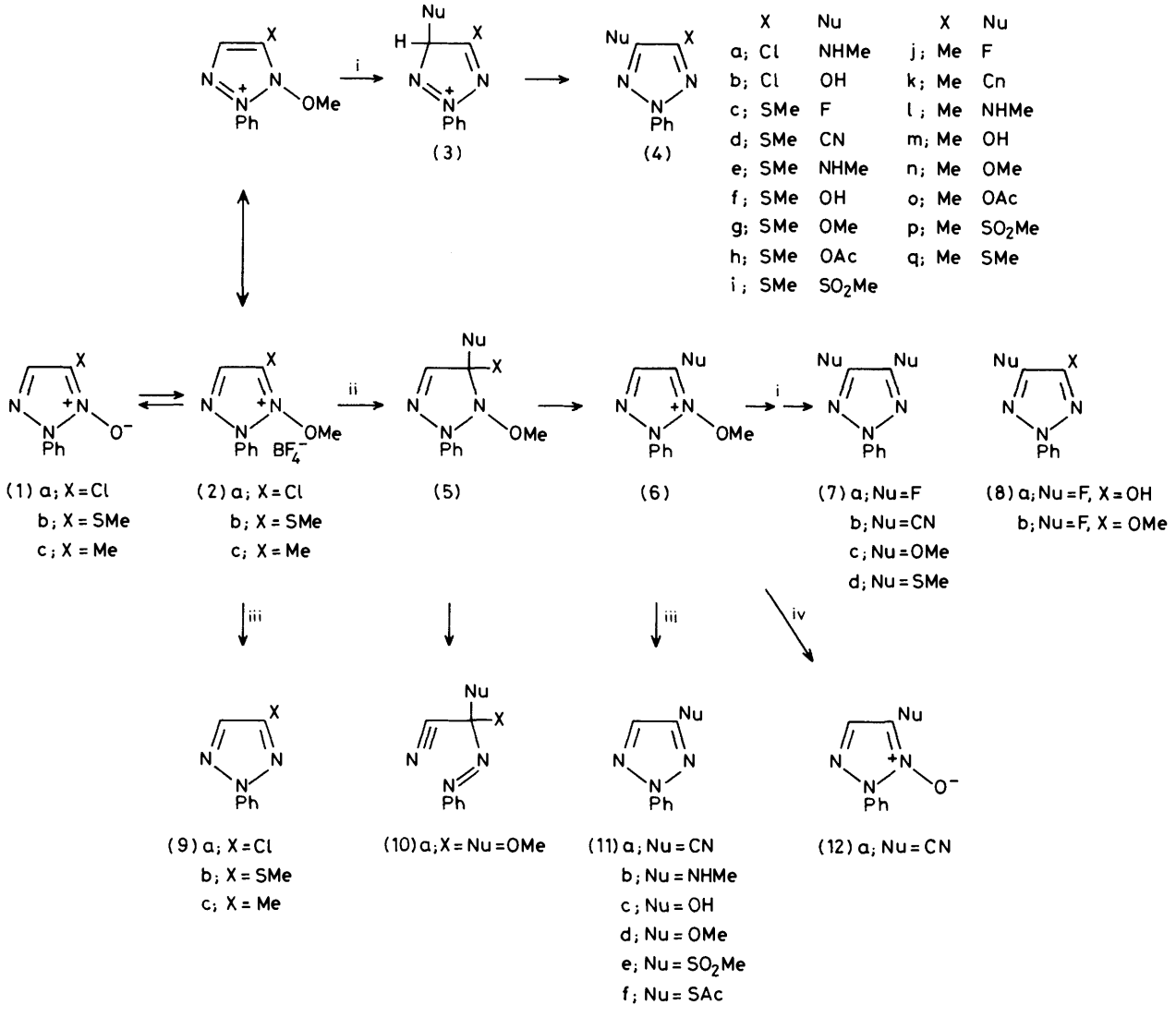
Reaction path (ii) does not seem to have been observed in other *N*-methoxy-substituted heteroaromatics either. It involves nucleophilic addition to the substituted ring carbon atom of compound (2) followed either by elimination of methanol with ring cleavage to give the azo-compound (10) or by elimination of the substituent X. The latter process gives rise to a novel 5-substituted triazolium salt (6) which, in its turn, may react further with a second mole of nucleophile along the four aforementioned paths (i—iv). If terminated by (i), a triazole (7) with two identical substituents results. This sequence is of preparative interest since only a few triazoles of this kind, mainly dihalogeno-derivatives, are known.[3] Two different nucleophiles may be introduced if the 1-methoxytriazolium salt (2) is treated with two nucleophiles, the first tailored to react with displacement of X in (2) to give the cation (6) and the second tailored to add to C-4 of (6) thus producing the neutral compound (8).

If the sequence (2) ⟶ (6) is terminated by reaction mode (iv), a 5-substituted triazole *N*-oxide (12) arises. This sequence is also of preparative interest, particularly since it makes the introduction of weak nucleophiles into triazole *N*-oxides possible. So far we have only been able to introduce strong nucleophiles.[1]

The sequence (2) ⟶ (6) may also be followed by repeated nucleophilic addition to C-5 of compound (6), producing the dihydro-compound (5; X = Nu), which either eliminates methanol with ring cleavage affording the cyanide (10; X = Nu), or eliminates X. The latter event is unrecognizable since the leaving group and nucleophile are identical.

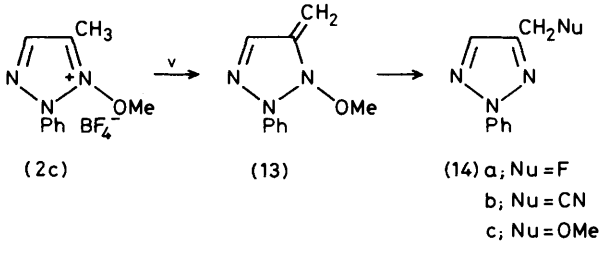
If the sequence (2) ⟶ (6) is terminated by reaction mode (iii), a monosubstituted triazole (11) is the final product. This is, however, more easily accessible from triazole *N*-oxides (1; X = H) or 1-methoxytriazolium salts (2; X = H) which are devoid of substituents at C-5.[1]

Reaction mode (v) (Scheme 2) has a parallel in the reaction of 2-methylpyridine 1-oxide with acyl or sulphonyl chloride



Scheme 1

to give acyloxymethyl- and chloromethyl-pyridine.[2c,4] It may occur in 1-methoxytriazolium salts possessing a substituent with an α-proton at C-5, as in the 5-methyltriazolium salt (2c). The α-protons of (2c) are acidic since their abstraction leads to a neutral species (13). This contains a C=CNOMe moiety which is susceptible to nucleophilic attack at its β-position with concomitant loss of methoxide ion and formation of the triazole (14).



Scheme 2

Results and Discussion

The 1-methoxytriazolium salts (2a—c) were treated with methylamine, alkali-metal fluoride, cyanide, acetate, methanesulphinate, methanethiolate, thioacetate, hydroxide, or methoxide as nucleophiles. Acetonitrile was used as the solvent, except for sodium hydroxide (water) and sodium methoxide (methanol). All the modes of reaction (i–v) discussed were encountered. Frequently two or more reaction paths compete. The course of a given transformation depends on the nature of the substituent in the salt (2) as well as that of the nucleophile. The influence of other factors such as the nature of the solvent and of the cation of the ionic nucleophiles is not included in the discussion, the aim being to unravel certain trends in the selectivity of the reactions rather than to optimize these with regard to a single compound. The individual reaction types are discussed below and the results summarized in Tables 1 and 2.

Displacement of the Substituent at the 5-Carbon.—The extent to which displacement of the 5-substituent of compound (2) occurs depends primarily on the nature of the leaving group (Table 1). With chlorine, a good leaving group, displacement to give 5-substituted 1-methoxytriazolium

Table 1. Reaction modes on the treatment of 5-chloro-, 5-methylthio-, and 5-methyl-1-methoxytriazolium tetrafluoroborate (2a—c) with nucleophiles

Starting material	Initial reaction mode [a]	Nucleophile / Product [% yield]								
		F^-	CN^-	NH_2Me	HO^-	MeO^-	AcO^-	$MeSO_2^-$	MeS^-	AcS^-
(2a)	(i)			(4a) [3]	(4b) [3]					
		(7a) [14]	(11a) [11]	(11b) [21]		(7c) [39]		(11e) [42]	(7d) [43]	(11f) [19]
	(ii)		(12a) [46]						(9b) [25]	
	(iii)		(2a) [3]		(9a) [22]		(9a) [12]			
	(iv)	(1a) [44]	(1a) [34]	(1a) [11]	(1a) [47]	(1a) [6]	(1a) [49]	(1a) [34]	(1a) [10]	(1a) [60]
	Other products	(8a) [2] (8b) [14]				(10a) [39]				
(2b)	(i)	(4c) [13]	(4d) [5]	(4e) [14]	(4f) [27]	(4g) [41]	(4h) [20]	(4i) [21]	(7d) [23]	
	(ii)		(7b) [7] (11a) [36]	(11b) [8]	(11c) [16]	(7c) [2] (10c) [20]				
	(iii)			(9b) [33]	(9b) [18]			(9b) [29]	(9b) [73]	(9b) [49]
	(iv)	(1b) [53] (4g) [5]	(1b) [22] (7d) [5]	(1b) [35]	(1b) [3] (4g) [6]	(1b) [3]	(1b) [52] (4g) [13]	(1b) [32] (11; Nu = SOMe [13]	(1b) [35]	(1b) [20]
(2c)	(i)	(4j) [7]	(4k) [30]	(41) [61]	(4m) [7]	(4n) [7]	(4o) [49]	(4p) [28]	(4q) [29]	
	(iii)	(9c) [6]	(9c) [3]	(9c) [3]	(9c) [59]	(9c) [36]	(9c) [23]	(9c) [32]	(9c) [30]	(9c) [65]
	(iv)		(1c) [35]	(1c) [16]			(1c) [18]			(1c) [23]
	(v)	(14a) [3]				(14c) [12]				
	Other products	(4n) [3] (14c) [2]			(4n) [8] (13c) [10]					(4n) [6]

[a] (i) Addition to C-4; (ii) replacement of the 5-substituent; (iii) deprotonation–elimination; (iv) dealkylation; (v) deprotonation of the 5-methyl group followed by nucleophilic addition.

Table 2. Reaction modes by reaction of the 5-substituted 1-methoxytriazolium ions (6) with a nucleophile identical with their 5-substituent

5-Substituent	F	Cl	CN		NHMe		OMe		SO_2Me		SMe		SAc
Nucleophile	F^-	Cl^-	CN^-		$MeNH_2$		MeO^-		$MeSO_2^-$		MeS^-		AcS^-
Starting material	(2a)	(2a)	(2a),	(2b)	(2a),	(2b)	(2a),	(2b)	(2a),	(2b)	(2a),	(2b)	(2a)
Reaction mode [a]	Deduced yields (% relative)												
(i)	100	0	0	100	0	0	100	19	0	0	63	24	0
(iii)	0	0	19	0	100	100	0	81	100	100	37	76	100
(iv)	0	100	81	0	0	0	0	0	0	0	0	0	0

[a] (i) Addition to C-4; (ii) replacement of the 5-substituent; (iii) deprotonation–elimination; (iv) dealkylation; (v) deprotonation of the 5-methyl group followed by nucleophilic addition.

salts (6) as the initial products is the sole or predominant process with most nucleophiles, including the fluoride ion. In contrast, displacement of the 5-methylthio-group of the salt (2b) is observed only when strong nucleophiles are employed and does not occur when methylamine, or acetate or fluoride ions are used. The displacement products (6), derived from the 5-chloro- (2a) or the 5-methylthio-1-methoxytriazolium salt (2b), react with a second mole of nucleophile with addition to C-4, and one of the following steps then occurs: repeated nucleophilic additon to C-5 followed by ring cleavage to give compound (10); deprotonation–elimination (iii); or dealkylation (iv) (Table 2). These terminating steps which determine the product composition are discussed below under the corresponding headings.

Addition to the 4-Carbon.—The extent to which addition to C-4 takes place depends primarily on the nature of the 5-substituent, but also on the nature of the nucleophile. This is apparent both from the observed behaviour of the salts (2a—b) (Table 1) and from the deduced behaviour of the salts (6) derived from (2a—b) by initial displacement of the 5-substituent (Table 2).

Addition to C-4 of the 5-chlorotriazolium salt (2a) is observed only with methylamine, the yield of the resulting 4-chloro-5-methylaminotriazole (4a) being as low as 3%. Obviously displacement of chlorine and other competing reactions of compound (2a) prevail. In contrast, the 5-methylthiotriazolium salt (2b) reacts with addition to C-4 with all of the nucleophiles except thioacetate ions to give the 4-substituted 5-methylthiotriazoles (4c—i). Addition to C-4 seems most significant when strong nucleophiles are employed; thus, the 4-hydroxy-, 4-methoxy-, 4-methylsulphonyl-, and 4-methylthio-substituted 5-methylthiotriazole [(4f, g, i) and (7d), respectively] are accessible in moderate yields while yields of the 4-fluoro-, 4-cyano-, and 4-methylamino-derivatives (4c—e), respecitively, are low.

Reaction of the 5-methylthiotriazolium salt (2b) with fluoride, hydroxy, or acetate ions affords small amounts of the 4-methoxy-5-methylthiotriazole (4g). It is likekly that (4g) is formed by addition of methoxide ions to C-4 of the unchanged salt (2b). The requisite methoxide ions become available by the initial addition of nucleophile to C-4 of (2b).

The 5-methyltriazolium salt (2c) also is susceptible to nucleophilic attack at C-4. Thus, fair to good yields of 4-fluoro-, 4-cyano-, 4-methylamino-, 4-acetoxy-, 4-methylsulphonyl-, and 4-methylthio-substituted 5-methyltriazole (4 k, l, and o—q), respectively, are attainable, whereas hydroxide or methoxide ions in this case only give low yields of the addition products 4-hydroxy- and 4-methoxy-5-methyltriazole (4m and n).

Reaction of the 5-methyltriazolium salt (2c) with fluoride, hydroxide, or thioacetate ions gives rise to small amounts of

the 4-methoxy-5-methyltriazole (4n), again the result of addition of liberated methoxide ions to unchanged starting material (2c).

As mentioned above, the 5-chloro- and 5-methyl-thiotriazolium salts (2a and b) react with certain nucleophiles with displacement of the 5-substituent to give new 5-substituted triazolium salts (6) as intermediates. If these possess a good leaving group at C-5 (6; Nu = OCOMe, SO_2Me, or SCOMe) they do not undergo addition to C-4 (Table 2). However, all of the intermediates (6) possessing a poor leaving group, except (6; Nu = NHMe), are attacked at C-4 by a second mole of nucleophile to give the triazoles (7) with two identical substituents. Thus, the 5-methoxytriazolium salt (6; Nu = OMe) formed as an intermediate by treatment of the chlorotriazolium salt (2a) with methoxide ions produces the dimethoxytriazole (7c). Dimethylthiotriazole (7d), the dicyanotriazole (7b), and difluorotriazole (7a) are formed in this way.

The intermediate (6) may also be attacked at C-4 by a different nucleophile to that from which it was formed. This sequence accounts for the production of the 4-fluoro-5-hydroxytriazole (8a) and the 4-fluoro-5-methoxytriazole (8b) by the reaction of the chlorotriazolium salt (2a) with fluoride ions (Table 1). Thus, (8a) may arise by addition of hydroxide ions from contaminating water to C-4 of the initially formed 5-fluorotriazolium salt (6; Nu = F). Similarly, (8b) may arise by addition of liberated methoxide ions to the same salt. The scope of this potentially useful method of introducing two different nucleophiles into the triazole nucleus has not been further investigated.

Apparently, the fate of a given intermediate (6) may depend on which precursor has been used for its generation (Table 2). Thus, addition to C-4 of the intermediate 5-cyanotriazolium salt (6; Nu = CN) was observed if this salt was generated from the 5-methylthiotriazolium salt (2b), but not if it was generated from the 5-chlorotriazolium salt (2a). This may be due to the influence of the liberated leaving group which competes with the original nucleophile, leading to an alternative transformation of the intermediate (6).

The fact that fluoride ions react sluggishly with the 5-methylthiotriazolium salt (2b), but quantitatively at C-4 of the intermediate 5-fluorotriazolium ion (6; Nu-F) producing the 4,5-difluorotriazole (7a), must be caused by activation of C-4 in the intermediate (6; Nu = F) by the strongly electron-attracting fluorine at C-5. Similar reasoning applies to the formation of the dicyanotriazole (7b).

To summarize, nucleophilic addition to C-4 of 5-substituted 1-methoxytriazolium salts, with few exceptions, is facilitated if the salts possess a poor leaving group which is electron-attracting, and if the nucleophile is strong.

Deprotonation of the 5-Methyl Group followed by Nucleophilic Addition.—Of the nucleophiles employed, only fluoride, cyanide, and methoxide ions were found to react with the 5-methyltriazolium salt (2c); this involved deprotonation of the 5-methyl group, followed by nucleophilic addition, to give 5-fluoromethyl-, 5-cyanomethyl-, and 5-methoxymethyltriazole (14a—c) in fair yields (Table 1).

The reaction of the salt (2c) with fluoride or hydroxy ions produces small amounts of the 4-methoxymethyltriazole (14c) as a by-product. Again, this product is accounted for by the addition of liberated methoxide ions to unchanged starting material.

No relation between the basicity, strength, or softness [5] of the nucleophile and its ability to react with deprotonation–addition is apparent.

Deprotonation-Elimination of Formaldehyde.—The extent to which deprotonation of the *N*-methoxy-group with subsequent elimination of formaldehyde takes place depends primarily on the nature of the leaving group. Generally, the tendency to undergo deprotonation–elimination decreases in the order 5-methyl-, 5-methylthio-, and 5-chloro-triazolium salt (2c, b, and a, respectively) (Table 1). The role of the nucleophile is less obvious, but cyanide ions seem less effective in inducing deprotonation–elimination.

From a preparative point of view, deprotonation–elimination is the least interesting of the three processes (i—iii). The data (Table 2) reveal that the intermediate 5-hydroxy-, 5-methylsulphonyl-, and 5-acetylthio-triazolium ions (6; Nu = OH, SO_2Me, or SCOMe, respectively) react with a second mole of the nucleophile, exclusively by deprotonation–elimination, producing 4-hydroxy-, 4-methylsulphonyl-, and 4-acetylthio-triazole (11c, e, and f), respectively. The 5-cyanotriazolium ion (6; Nu = CN) undergoes the same reaction to a minor extent to give 4-cyanotriazole (11a), whilst the 5-fluoro-, 5-methylamino-, 5-methoxy-, and 5-acetoxy-triazolium ions (6; Nu = F, NHMe, OMe, or OCOMe, respectively) do not. The data of Table 2 are insufficient to provide a basis for further generalizations.

Dealkylation.—The extent to which dealkylation of 1-methoxytriazolium salts (2) takes place is dependent on the nature of the 5-substituent (Table 1). Generally, the tendency to undergo dealkylation increases in the order 5-methyl-, 5-methylthio-, and 5-chloro-triazolium salts (2c—a), *i.e.* opposite that favouring the deprotonation–elimination reaction.

From a preparative point of view, dealkylation is of interest when it terminates a sequence initiated by displacement of chlorine or the methylthio-group in the triazolium salts (2a and b). However, in these cases dealkylation is only observed in the reaction of 5-cyanotriazolium ion (6; Nu = CN) with an excess of cyanide ions to give the 5-cyanotriazole 1-oxide (12a) (Scheme 1).

Ring Cleavage.—The only ring-cleavage product to be isolated and characterized was benzeneazodimethoxyacetonitrile (10a) (see Experimental section). It was formed in 39% yield by treatment of the chlorotriazolium salt (2a) with sodium methoxide. It is likely that compound (10a) arises by displacement of the chlorine in the salt (2a) with methoxide to give the intermediate (6; Nu = OMe). Repeated addition to C-5 produces compound (5; X = Nu = OMe) which, upon elimination of methanol, affords (10a).

Experimental

Solvents were removed under reduced pressure. Flash chromatography was performed as described in ref. 6. The purity and identity of all compounds were confirmed using t.l.c., the m.p., and the i.r., ^1H n.m.r., and mass spectra. ^1H and ^{19}F N.m.r. spectra were recorded on a Bruker HX-90 instrument. ^{13}C N.m.r. spectra were obtained on a Bruker WH-90 instrument and assigned as described previously.[1] Mass spectra were obtained on a V.G. Micromass 7090 F instrument.

Preparation of Triazole N-*Oxides.*—(*a*) 2-Hydroxyiminopropanal [7] was treated with phenylhydrazine as described for nitrosoacetone [1] to give 2-hydroxyimino-1-phenylhydrazonopropane (68%), m.p. 149—150 °C; this was oxidized with cupric ions [1] to give *5-methyl-2-phenyl*-1,2,3-*triazole* 1-*oxide* (1c) (81%) as colourless crystals, m.p. 57—59 °C (ethyl acetate–hexane) (Found: C, 61.6; H, 5.1; N, 23.9. $C_9H_9N_3O$ requires C, 61.7; H, 5.2; N, 24.0%); *m/e* 175 (90%, M^+), 159 (7, $M - O$), 118 (14), 91 (61, C_6H_5N), 77 (100, C_6H_5), and 51 (26). ^1H and ^{13}C N.m.r. data are given in ref. 1.

(*b*) Alternatively, methylglyoxal was treated, like glyoxal,[1]

Table 3. Yields, m.p.s, and analytical data of the 1-methoxy-1,2,3-triazolium tetrafluoroborates (2a—c)

Starting material	Product	Yield (%)	M.p. (°C)	Found (Calc.) (%)	δ (CD_3CN)
(1c)	(2c)	98	91—92	C, 42.9 (43.35); H, 4.3 (4.35); N, 15.1 (15.5)	*a*
(1a)[1]	(2a)	100	124—127	C, 35.0 (36.35); H, 3.05 (3.05); Cl, 11.7 (11.9);[b] N, 13.4 (14.15)	8.55 (4-H), 7.83 (Ph), 4.28 (OMe)
(1b)[1]	(2b)	100	139—141	C, 38.6 (38.85); H, 3.9 (3.9); N, 13.45 (13.6)	8.34 (4-H), 7.77 (Ph), 4.17 (OMe), 2.87 (SMe)

[a] Data published previously (see ref. 1). [b] The compound is very hygroscopic and therefore a correct analysis could not be obtained.

with phenylhydrazine to give a crude product which was flash chromatographed (dichloromethane) to produce 2-phenylhydrazonopropanol (20%), identical with the material described previously.[8] Subsequent elution with ethyl acetate gave 1-phenylhydrazonopropanone (64%) as yellow crystals, m.p. 149 °C (lit.,[9] 148—149 °C). The latter compound was treated with hydroxylamine as described for phenylhydrazonoethanal,[1] except that the reaction mixture was kept for 3 d before work-up, to give 2-hydroxyimino-1-phenylhydrazonopropane (66%), which was oxidized as described above.

(*c*) 2-Phenylhydrazonobutan-3-one [10] was treated, like 1-phenylhydrazonopropanone in (*b*), with hydroxylamine to give 3-hydroxyimino-2-phenylhydrazonobutane (70%), m.p. 137—140 °C (lit.,[11] 158 °C) which was oxidized as above to yield 4,5-dimethyl-2-phenyl-1,2,3-triazole 1-oxide (94%), m.p. 90—92 °C (lit.,[12] 92—93 °C) (Found: C, 63.7; H, 5.95; N, 22.1. $C_{10}H_{11}N_3O$ requires C, 63.5; H, 5.65; N, 22.2%); *m/e*, 189 (77%, M^+), 173 (7, $M - O$), 122 (20), 91 (100, C_6H_5N), 77 (83, C_6H_5), and 51 (21); δ ($CDCl_3$) 8.0—7.8 and 7.6—7.3 (2 H, m, and 3 H, m, Ph), and 2.28 (6 H, s, 2 Me); δ_C ($CDCl_3$) 140.2 (C-5), 135.1 (C-4 and -1′), 128.7 (C-3′), 128.2 (C-4′), 122.3 (C-2′), 11.4 (4-Me), and 7.3 (5-Me).

Preparation of 1-*Methoxytriazolium Salts.*—This was accomplished by treatment of 2-phenyltriazole 1-oxide (1) with trimethyloxonium tetrafluoroborate, as described previously.[1] Yields, m.p., and analytical, and n.m.r. data are given in Table 3.

Reactions of 1-*Methoxytriazolium Salts with Nucleophiles.*—*General.* All solid nucleophiles used were finely ground and dried (P_2O_5 at 1.3 Pa). Acetonitrile was purified [13] and dried over molecular sieves (3 Å). Methanol was distilled from magnesium. Moisture was excluded during the reactions.

Reactions with Fluoride Ions.—(*a*) 5-Chloro-1-methoxy-2-phenyl-1,2,3-triazolium tetrafluoroborate (2a) (0.40 g), potassium hydrogen fluoride (1.09 g), and acetonitrile (4.0 ml) were stirred for 7 d. The acetonitrile was removed and the residue extracted with dichloromethane (3 × 5 ml). Removal of the dichloromethane and flash chromatography (hexane) gave 4,5-*difluoro*-2-*phenyl*-1,2,3-*triazole* (7a) (34 mg, 14%) as very volatile, colourless crystals, m.p. 74 °C. Sublimation at 10^5 Pa did not raise the m.p. (Found: C, 53.45; H, 2.7; N, 22.85. $C_8H_5N_3F_2$ requires C, 53.05; H, 2.8; N, 21.0%); *m/e* 181 (100%, M^+); δ ($CDCl_3$) 7.95—7.7 and 7.6—7.25 (2 H, m, and 3 H, m, Ph); δ_F ($CDCl_3$–$CFCl_3$) 152.1 [J_{FF} 5.2 Hz, J_{CF} 251 Hz, (coupling constants from a first-order analysis of the ^{13}C satellites in the ^{19}F n.m.r. spectrum)]. The next fraction contained 4-*fluoro*-5-*methoxy*-2-*phenyl*-1,2,3-*triazole* (8b) (37 mg, 14%) obtained as a colourless oil, crystalline below 0 °C (Found: C, 55.45; H, 3.95; N, 22.05. $C_9H_8FN_3O$ requires C, 55.95; H, 4.15; N, 21.75%); *m/e* 193 (100%, M^+); δ ($CDCl_3$) 7.9—7.7 and 7.55—7.2 (2 H, m, and 3 H, m, Ph), and 4.06 (3 H, s, OMe); δ_F ($CDCl_3$–$CFCl_3$) 152.6. Subsequent elution with ethyl acetate–hexane (1 : 4) gave a mixture (28 mg) which, by preparative t.l.c. (ethyl acetate–hexane, 1 : 10), gave a colourless oil (2 mg, 1%) (R_F 0.73) which was assumed to be bis(5-fluoro-2-phenyl-1,2,3-triazol-4-yl) ether; * δ ($CDCl_3$) 7.95—7.75 and 7.55—7.2 (4 H, m, and 6 H, m, 2 Ph); [Found: M^+, 340.085 (74%). $C_{16}H_{10}F_2N_6O$ requires *M*, 340.088]. A second fraction (R_F 0.10) contained colourless crystals (5 mg, 2%), m.p. 146—150 °C, believed to be 4-fluoro-5-hydroxy-2-phenyl-1,2,3-triazole (8a); δ ($CDCl_3$) 7.8—7.6 and 7.55—7.15 (2 H, m, and 3 H, m, Ph); δ_F ($CDCl_3$–$CFCl_3$) 154.1 (s) [Found: M^+, 179.048 (57%). $C_8H_6FN_3O$ requires *M*, 179.050]. The last fraction from the column contained 5-chloro-2-phenyltriazole 1-oxide (1a) (0.12 g, 44%), identical with the material described previously.[1]

(*b*) Similarly, 1-methoxy-5-methylthio-2-phenyl-1,2,3-triazolium tetrafluoroborate (2b) (0.29 g) gave a crude product which was flash chromatographed (hexane) to give 4-*fluoro*-5-*methylthio*-2-*phenyl*-1,2,3-*triazole* (4c) (25 mg, 13%) as a colourless oil, crystalline below −20 °C (Found: C, 51.9; H, 3.75; N, 20.45. $C_9H_8FN_3S$ requires C, 51.65; H, 3.85; N, 20.1%); *m/e* 209 (100%, M^+); δ ($CDCl_3$) 8.0—7.8 and 7.55—7.2 (2 H, m, and 3 H, m, Ph), and 2.56 (3 H, s, SMe); δ_F ($CDCl_3$–$CFCl_3$) 142.3. The column was then eluted with dichloromethane to give 4-methoxy-5-methylthio-2-phenyltriazole (4g) (11 mg, 5%), identical with the material described below. Subsequent elution with ethyl acetate–hexane (1 : 4) gave the methylthiotriazole 1-oxide (1b) (0.10 g, 53%), identical with the material described previously.[1]

(*c*) Analogously, 1-methoxy-5-methyl-2-phenyl-1,2,3-triazolium tetrafluoroborate (2c) (0.14 g) gave a crude product which was flash chromatographed (dichloromethane–hexane, 1 : 2) to give 4-fluoro-5-methyl-2-phenyltriazole (4j) (7 mg, 7%), described previously.[1] Subsequent elution with dichloromethane gave a fraction containing two compounds which were separated by preparative t.l.c. (ether–hexane, 1 : 5) to give 4-methoxy-5-methyl-2-phenyltriazole (4n) (3 mg, 3%) (R_F 0.69), described previously,[1] and 4-*fluoromethyl*-2-*phenyl*-1,2,3-*triazole* (14a) (3 mg, 3%) (R_F 0.54), as a colourless oil [Found: M^+, 177.070 (18%). $C_9H_8FN_3$ requires *M*, 177.070]; δ ($CDCl_3$) 8.15—7.95 and 7.6—7.1 (2 H, m, and 3 H, m, Ph), 7.39 (1 H, s, H-5), and 5.53 (2 H, d, *J* 47.8 Hz, CH_2F); δ_F ($CDCl_3$–$CFCl_3$) 102.5 (t, *J* 47.8 Hz). The column was then eluted with ethyl acetate–hexane (1 : 4) to give 4-methyl-2-phenyltriazole (9c) (5 mg, 6%), described previously,[14] and 4-methoxymethyl-2-phenyltriazole (14c) (2 mg, 2%), described below.

Reaction with Cyanide Ions.—(*a*) The 5-chloro-1-methoxy-

* The bis-triazolyl ether is probably an artefact arising from addition of the fluorohydroxytriazole (8a) to C-4 of compound (6; Nu = F). A similar reaction involving the non-fluorinated analogues has been observed.[1]

triazolium salt (2a) (0.17 g), potassium cyanide (83 mg), and acetonitrile (1.7 ml) were stirred together for 3 d. The acetonitrile was removed and the residue extracted with dichloromethane (4 × 4 ml). Removal of the solvent and flash chromatography (dichloromethane–hexane, 1 : 1) gave 4-chloro-2-phenyltriazole (9a) (4 mg, 3%) and 4-cyano-2-phenyltriazole (11a) (10 mg, 11%), both identical with the compounds described previously.[1] The column was then eluted with dichloromethane to give *5-cyano-2-phenyl*-1,2,3-*triazole* 1-*oxide* (12a) (49 mg, 46%) as colourless crystals, m.p. 117—118 °C. Recrystallization (ethyl acetate–hexane) gave m.p. 130—131 °C (Found: C, 57.95; H, 3.25; N, 30.2. $C_9H_6N_4O$ requires C, 58.05; H, 3.25; N, 30.1%); *m/e* 186 (84%, M^+), 171 (2), 170 (13, $M - O$), 91 (21, $M - C_6H_5N$), 77 (100, C_6H_5), and 51 (25); δ ($CDCl_3$) 7.97 (1 H, s, H-4), and 7.95—7.75 and 7.6—7.4 (2 H, m, and 3 H, m, Ph). The next fraction contained 5-chloro-2-phenyltriazole 1-oxide (1a) (38 mg, 34%), identical with the material described previously.[1]

(*b*) The 1-methoxy-5-methylthiotriazolium salt (2b) (0.27 g) and potassium cyanide (0.14 g) in acetonitrile (2.8 ml) similarly, after flash chromatography (dichloromethane–hexane, 1 : 4), gave 4,5-bis(methylthio)-2-phenyltriazole (7d), (10 mg, 5%), identical with the compound described below. The next fraction contained 4-*cyano-5-methylthio-2-phenyl*-1,2,3-*triazole* (4d) (10 mg, 5%) as colourless crystals, m.p. 63—65 °C. (Dissolution in hexane, filtration through activated carbon, and removal of the hexane did not change the m.p.) [Found: M^+, 216.040 (100%). $C_{10}H_8N_4S$ requires *M*, 216.047]; δ ($CDCl_3$) 8.05—7.9 and 7.5—7.25 (2 H, m, and 3 H, m, Ph), and 2.70 (3 H, s, Me). The next fraction contained a mixture which, upon preparative t.l.c. (dichloromethane–hexane, 1 : 4), gave 4-methylthio-2-phenyltriazole (9b) (8 mg, 5%) (R_F 0.31), described previously,[1] and 4,5-*dicyano-2-phenyl*-1,2,3-*triazole* (7b) (12 mg, 7%) (R_F 0.17) as colourless crystals, m.p. 139—141 °C [Found: C, 62.35; H, 2.75; N, 35.15%; M^+,195.054 (100%) $C_{10}H_5N_5$ requires C, 61.55; H, 2.55; N, 35.9%; *M*, 195.054; δ ($CDCl_3$) 8.2—7.95 and 7.65—7.4 (2 H, m, and 3 H, m, Ph). The next fraction from the column contained 4-cyano-2-phenyltriazole (11a) (38 mg, 26%), described previously.[1] The column was then eluted with ether–hexane (1 : 1) to give the methylthiotriazole 1-oxide (1b) (41 mg, 22%), described previously.[1]

(*c*) The 1-methoxy-5-methyltriazolium salt (2c) (0.22 g), potassium cyanide (0.11 g), and acetonitrile (2.2 ml) similarly, after preparative t.l.c. (ethyl acetate–hexane, 1 : 4), gave 4-*cyano-5-methyl-2-phenyl*-1,2,3-*triazole* (4k) (44 mg, 30%) (R_F 0.48), colourless crystals, m.p. 109—113 °C. Recrystallization (hexane) gave m.p. 117—118 °C (Found: C, 65.3; H, 4.35; N, 30.9. $C_{10}H_8N_4$ requires C, 65.2; H, 4.4; N, 30.4%); *m/e* 184 (100%, M^+); δ ($CDCl_3$) 8.1—7.85 and 7.6—7.3 (2 H, m, and 3 H, m, Ph), and 2.50 (3 H, s, Me). The next two fractions (12 mg, R_F 0.62 and 34 mg, R_F 0.37) contained unidentified compounds. The last fraction contained the 5-methyltriazole 1-oxide (1c) (50 mg, 35%) (R_F 0.08), described above.

Reaction with Methylamine.—(*a*) Methylamine, distilled from calcium sulphate, was condensed in a flask with the 5-chloro-1-methoxytriazolium salt (2a) (0.36 g). Acetonitrile (1.8 ml) was added and the mixture kept at 20 °C for 3 d. It was then evaporated to dryness and extracted with dichloromethane (3 × 5 ml), and the solvent was removed to give a residue which was subjected to preparative t.l.c. (ethyl acetate–hexane, 1 : 6). The first fraction (R_F 0.62) contained 4-*chloro-5-methylamino-2-phenyl*-1,2,3-*triazole* (4a) (7 mg, 3%) as a colourless oil [Found: M^+, 208.050 (100%). $C_9H_9ClN_4$ requires *M*, 208.052]; *m/e* 210 (32%, $M + 2$); δ ($CDCl_3$) 8.0—7.75 and 7.5—7.05 (2 H, m, and 3 H, m, Ph), and 2.95 (4 H, s, 1 H exchangeable, NH and Me). The next fractions contained 4-methylamino-2-phenyltriazole (11b) (45 mg, 21%) (R_F 0.39) and the chlorotriazole 1-oxide (1a) (26 mg, 11%) (R_F 0.32), both identical with the compounds described previously.[1]

(*b*) Similarly, the 1-methoxy-5-methylthiotriazolium salt (2b) (0.24 g) and methylamine in acetonitrile, after flash chromatography (dichloromethane) gave 4-methylthio-2-phenyltriazole (9b) (50 mg, 33%), identical with the compound described previously.[1] The next fraction contained 4-*methylamino-5-methylthio-2-phenyl*-1,2,3-*triazole* (4e) (24 mg, 14%) as a colourless oil. Reprecipitation (hexane) gave the pure compound [Found: M^+, 220.080 (100%). $C_{10}H_{12}N_4S$ requires *M*, 220.078]; δ ($CDCl_3$) 8.0—7.8 and 7.5—7.15 (2 H, m, and 3 H, m, Ph), 3.83 (1 H, br s, NH), 3.03 (3 H, d, *J* 5.3 Hz, collapses on irradiation at 3.83, NMe), and 2.42 (3 H, s, SMe). Subsequent elution with ethyl acetate–hexane (1 : 6) gave 4-methylamino-2-phenyltriazole (11b) (10 mg, 8%) and then the methylthiotriazole 1-oxide (1b) (55 mg, 35%). Both compounds were identical with materials described previously.[1]

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (0.28 g) and methylamine in acetonitrile after flash chromatography (dichloromethane–hexane, 1 : 2) gave a minute amount of 4-methoxy-5-methyl-2-phenyltriazole (4n), described previously.[1] The next fraction contained 4-methyl-2-phenyltriazole (9c), (5 mg, 3%), identical with an authentic specimen.[13] Subsequent elution with ethyl acetate–hexane (1 : 4) afforded 4-methyl-5-methylamino-2-phenyltriazole (4l) (0.11 g, 61%), identical with the material described previously.[1] The last fraction contained the 5-methyltriazole 1-oxide (1c) (28 mg, 16%), described above.

Reaction with Hydroxide Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (0.32 g) was treated with 10% aqueous sodium hydroxide (11.1 ml) as described previously.[1] After being stirred for 1 d, the mixture was extracted with dichloromethane (3 × 3 ml). The dichloromethane was removed and the residue flash chromatographed (dichloromethane) to give 4-chloro-2-phenyltriazole (9a) (42 mg, 22%). Subsequent elution with ethyl acetate–hexane (1 : 4) yielded the chlorotriazole 1-oxide (1a) (99 mg, 47%). Both compounds were identical with those described previously.[1] The aqueous solution was acidified with concentrated hydrochloric acid, extracted with dichloromethane (3 × 5 ml), and the dichloromethane removed to give 4-*chloro-5-hydroxy-2-phenyl*-1,2,3-*triazole* (4b) (4 mg, 2%) as colourless crystals (chloroform), m.p. 151 °C (Found: C, 48.75; H, 2.95; Cl, 18.25, N, 21.65; $C_8H_6ClN_3O$ requires C, 49.1; H, 3.1; Cl 18.15; N, 21.5%); δ ($CDCl_3$) 10.25 (1 H, br s, exchangeable, OH), 7.85—7.6, and 7.6—7.25 (2 H, m and 3 H, m, Ph).

(*b*) Analogously, the 1-methoxy-5-methylthiotriazolium salt (2b) (0.10 g) gave a dichloromethane extract which, upon preparative t.l.c. (ethyl acetate–hexane, 1 : 4), gave a 3 : 1 mixture (16 mg) (R_F 0.77) (n.m.r.) of 4-methylthio-2-phenyltriazole (9b) and 4-methoxy-5-methylthio-2-phenyltriazole (4g) (18 and 6%, respectively). In addition, the methylthiotriazole 1-oxide (1b) (2 mg, 3%) (R_F 0.27) was obtained. The aqueous solution was acidified and extracted with dichloromethane. Removal of the solvent and flash chromatography (ethyl acetate–hexane, 1 : 5) afforded 4-*hydroxy-5-methylthio-2-phenyltriazole* (4f) (18 mg, 27%) as colourless crystals, m.p. 135—136 °C. Recrystallization (ethyl acetate–hexane) did not raise the m.p. (Found: C, 51.85; H, 4.25; N, 20.3; S, 15.35. $C_9H_9N_3OS$ requires C, 52.15; H, 4.4; N, 20.3; S, 15.45%); δ ($CDCl_3$) 10.25 (1 H, br s, exchangeable, OH), 7.85—7.7 and 7.55—7.15 (2 H, m, and 3 H, m, Ph), and 2.56 (3 H, s, Me). The next fraction contained 4-hydroxy-2-phenyltriazole (11c) (9 mg, 11%), described previously.[1]

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (0.13 g) gave a dichloromethane extract which contained a 1 : 7.7 : 1.3 mixture (70 mg) (n.m.r.) of 4-methyl-5-methoxy-2-phenyltriazole (4n),[1] 4-methyl-2-phenyltriazole (9c),[14] and 4-methoxymethyl-2-phenyltriazole (14c),[1] in 8, 59, and 10% yields, respectively. The acidified aqueous solution, after extraction with dichloromethane and removal of the solvent, gave 4-hydroxy-5-methyl-2-phenyltriazole (4m), (6 mg, 7%) described previously.[1]

Reaction with Methoxide Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (0.50 g) and 1M sodium methoxide in methanol (3.7 ml) were stirred for 1 d. The methanol was removed and the residue extracted with dichloromethane (4 × 5 ml); the dichloromethane was then removed and the residue flash chromatographed (ethyl acetate–hexane, 1 : 10) to give 4,5-*dimethoxy*-2-*phenyl*-1,2,3-*triazole* (7c) (0.14 g, 39%) which crystallized on cooling, m.p. 63—65 °C. Recrystallization (hexane) did not raise the m.p. (Found: C, 58.75; H, 5.55; N, 20.5. $C_{10}H_{11}N_3O_2$ requires C, 58.55; H, 5.4; N, 20.5%); *m/e* 205 (100%, M^+); δ ($CDCl_3$) 7.85—7.65 and 7.5—7.0 (2 H, m, and 3 H, m, Ph), and 4.03 (6 H, s, 2 Me); δ_C ($CDCl_3$) 148.3 (C-4 and C-5), 140.1 (C-1′), 128.9 (C-3′), 124.5 (C-4′), 116.0 (C-2′), and 57.5 (Me). The ^1H and ^{13}C n.m.r. shifts of the methyl group of compound (7c) are similar to those (4.00 and 59.6 p.p.m.) of the methyl group of 4-methoxy-2-phenyltriazole (11d).[1] In addition, the shift of C-4 [C-5 in (7c)] agrees reasonably well with that calculated (144.2 p.p.m.) using the substituent effect obtained by comparison of the hetero-ring carbon shift (139.4 p.p.m.) of 2-phenyltriazole (9; X = H) with those (C-4 162.1; C-5 121.5 p.p.m.) of its 4-methoxy-derivative (11d). The next fraction contained *benzene azodimethoxyacetonitrile* (10a) (0.14 g, 39%), a yellow oil, crystalline below *ca.* −20 °C. It was reprecipitated from hexane (Found: C, 58.8; H, 6.0. $C_{10}H_{11}N_3O_2$ requires C, 58.75; H, 5.55%); *m/e* 205 (36%, M^+); δ ($CDCl_3$) 8.0—7.75 and 7.6—7.35 (2 H, m, and 3 H, m, Ph), and 3.67 (6 H, s, 2 OMe); δ_C ($CDCl_3$) 150.0 (C-1′), 133.3 (C-4′), 129.2 (C-3′), 123.7 (C-2′), 112.4 (s) and 111.9 (s) (CN and C), and 52.6 (Me); $\nu_{max.}$ (CCl_4) 2 240 cm^{-1} (CN). Subsequent elution with ethyl acetate–hexane (1 : 4) gave the chlorotriazole 1-oxide (1a) (21 mg, 6%).

(*b*) Similarly, the 1-methoxy-5-methylthiotriazolium salt (2b) (0.37 g) gave a crude product which, upon flash chromatography (dichloromethane–hexane, 1 : 2) afforded 4-*methoxy*-5-*methylthio*-2-*phenyl*-1,2,3-*triazole* (4g) (0.11 g, 41%) as a colourless oil, m.p. *ca.* 18 °C. Low temperature recrystallization (hexane) gave m.p. 21 °C (Found: C, 54.65; H, 5.1; N, 19.15. $C_{10}H_{11}N_3OS$ requires C, 54.3; H, 5.0; N, 19.0%); *m/e* 221 (100%, M^+); δ ($CDCl_3$) 7.95—7.75 and 7.5—7.1 (2 H, m, and 3 H, m, Ph), 4.05 (3 H, s, OMe), and 2.52 (3 H, s, SMe). The next fraction contained a 1 : 4.4 mixture (16 mg) of 4,5-dimethoxy-2-phenyltriazole (7c) and 4-methoxy-2-phenyltriazole (11d) (2 and 7%, respectively). The compounds were identified by ^1H n.m.r. with addition of the pure substances to the solution. The next fraction contained pure compound (11d) (28 mg, 13%). Subsequent elution with ethyl acetate—hexane (1 : 4) gave the methylthiotriazole 1-oxide (1b) (7 mg, 3%).

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (0.16 g) yielded a crude product which, upon preparative t.l.c. (ethyl acetate–hexane, 1 : 10), gave 4-methoxy-5-methyl-2-phenyltriazole (4n) (8 mg, 7%) (R_F 0.54) and 4-methyl-2-phenyltriazole (9c) (34 mg, 36%) (R_F 0.47), both described previously.[1,13] The next fraction (R_F 0.30) gave 4-*methoxy*, *methyl*-2-*phenyl*-1,2,3-*triazole* (14c) (14 mg, 12%) as a yellow oil which was reprecipitated from hexane [Found: M^+, 189.090 (100%). $C_{10}H_{11}N_3O$ requires *M*, 189.090]; δ ($CDCl_3$) 7.76 (1 H, s, 5-H), 8.1—7.9 and 7.6—7.25 (2 H, m, and 3 H, m, Ph), 4.61 (2 H, s, CH_2), and 3.43 (3 H, s, Me).

Reaction with Acetate Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (55 mg), potassium acetate (40 mg), and acetonitrile (0.55 ml) were stirred together for 3 d and then heated to 80 °C for 3 h. The solvent was removed and the residue extracted with dichloromethane (4 × 5 ml); the dichloromethane was then removed and the residue flash chromatographed (ethyl acetate–hexane 1 : 10) to give 4-chloro-2-phenyltriazole (9a) (4 mg, 12%). Subsequent elution with ethyl acetate–hexane (1 : 4) gave the chlorotriazole 1-oxide (1a) (18 mg, 49%). Both compounds were identical with those described previously.[1]

(*b*) Similarly, the 1-methoxy-5-methylthiotriazolium salt (2b) (33 mg) gave a crude product which, upon preparative t.l.c. (dichloromethane–hexane, 1 : 2), gave 4-methoxy-5-methylthio-2-phenyltriazole (4g) (3 mg, 13%) (R_F 0.31), identical with the material described above, and 4-*acetoxy*-5-*methylthio*-2-*phenyl*-1,2,3-*triazole* (4h) (5 mg, 20%) (R_F 0.15) as colourless crystals, m.p. 51—52 °C (Found: C, 53.0; H, 4.85; N, 16.95; S, 13.05. $C_{11}H_{11}N_3O_2S$ requires C, 53.0; H, 4.45; N, 16.85; S, 12.85%); *m/e* 249 (10%, M^+); δ ($CDCl_3$) 8.0—7.85 and 7.55—7.25 (2 H, m, and 3 H, m, Ph), 2.55 (3 H, s, MeS), and 2.37 (3 H, s, MeCO). Finally, the methylthiotriazole 1-oxide (1b) [1] (12 mg, 52%) (R_F 0.02) was isolated from the t.l.c. plate.

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (21 mg) afforded 4-acetoxy-5-methyl-2-phenyltriazole (4o) (R_F 0.34) (8 mg, 49%), 4-methyl-2-phenyltriazole (9c) (R_F 0.23) (3 mg, 23%), and the 5-methyltriazole-1-oxide (1c) (2 mg, 18%) (R_F 0.08), all identical with the compounds described previously [1] or in ref. 14.

Reaction with Methanesulphinate Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (57 mg), sodium methanesulphinate [15] (77 mg), and acetonitrile (0.6 ml) were stirred together for 1 d and then heated to 80 °C for 3 h. The solvent was removed and the mixture extracted with dichloromethane (3 × 3 ml); removal of the dichloromethane and flash chromatography (ethyl acetate–hexane, 1 : 4) gave the chlorotriazole 1-oxide (1a) (13 mg, 34%) and 4-methylsulphonyl-2-phenyltriazole (11e) (18 mg, 42%), both identical with the compounds described previously.[1,*]

(*b*) The 1-methoxy-5-methylthiotriazolium salt (2b) (0.27 g) similarly, after preparative t.l.c. (dichloromethane), gave 4-methylthio-2-phenyltriazole (9b) (48 mg, 29%) (R_F 0.85), 4-methylsulphonyl-5-methylthio-2-phenyltriazole (4i) (49 mg, 21%) (R_F 0.46), 4-methylsulphonyl-2-phenyltriazole (11e) (22 mg, 11%) (R_F 0.36), and the methylthiotriazole 1-oxide (1b) (59 mg, 32%) (R_F 0.13), all of which were identical with those described previously.[1] The last fraction (R_F 0.03) contained a mixture (51 mg) which, on preparative t.l.c. (acetone–hexane, 1 : 1), yielded colourless crystals (23 mg, 13%), m.p. 60 °C (hexane); this was probably 4-methylsulphinyl-2-phenyl-1,2,3-triazole (11; Nu = SOMe) [Found: M^+, 207.045 (56%). $C_9H_9N_3OS$ requires *M*, 207.051]; δ ($CDCl_3$) 8.18 (1 H, s, 5-H), 8.15—7.9 and 7.65—7.3 (2 H, m, and 3 H, m, Ph), and 3.05 (3 H, s, Me).

(*c*) The 1-methoxy-5-methyltriazolium salt (2c) (0.15 g) likewise, after flash chromatography (dichloromethane–hexane, 1 : 2) gave 4-methyl-2-phenyltriazole (9c) (28 mg, 32%), identical with an authentic specimen,[14] and 4-*methyl*-5-

* This compound is a sulphone rather than a sulphinic ester since it is unchanged after heating under reflux for 3 h with an excess of sodium hydroxide in 33% aqueous methanol; these conditions lead to quantitative hydrolysis of the corresponding acyloxytriazoles.[1]

methylsulphonyl-2-phenyl-1,2,3-triazole (4p) (36 mg, 28%) as colourless crystals, m.p. 79—84 °C. Recrystallization (hexane) gave m.p. 89 °C (Found: C, 50.75; H, 4.75; N, 17.65. $C_{10}H_{11}N_3O_2S$ requires C, 50.6; H, 4.65; N, 17.7%); *m/e* 237 (100%, M^+); δ ($CDCl_3$) 8.1—7.9 and 7.6—7.35 (2 H, m, and 3 H, m, Ph), 3.28 (3 H, s, SMe), and 2.62 (3 H, s, CMe).

Reaction with Methanethiolate Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (57 mg), sodium methanethiolate [from a 55% suspension of sodium hydride in mineral oil (10 mg) and methanethiol [1]], and acetonitrile (0.7 ml) were stirred together for 3 d. The mixture was evaporated to dryness and extracted with dichloromethane (3 × 5 ml); the dichloromethane was removed and the residue flash chromatographed (dichloromethane–hexane, 1 : 2) to give *4,5-bis(methylthio)-2-phenyl-1,2,3-triazole* (7d) (20 mg, 43%) which crystallized on cooling, m.p. 27 °C. Dissolution in hexane, filtration through activated carbon, and recrystallization (methanol) did not raise the m.p. [Found: C, 50.15; H, 4.65; N, 17.3%; M^+, 237.040 (100%). $C_{10}H_{11}N_3S$ requires C, 50.6; H, 4.65; N, 17.7%; *M*, 237.039]; δ ($CDCl_3$) 8.05—7.85 and 7.55—7.2 (2 H, m, and 3 H, m, Ph), and 2.58 (6 H, s, 2 Me). The next fraction contained 4-methylthio-2-phenyltriazole (9b) (9 mg, 25%), described previously.[1] The column was then eluted with ethyl acetate–hexane (1 : 4) to give the 5-chlorotriazole 1-oxide (1a) (4 mg, 10%), described previously.[1]

(*b*) Similarly, the 1-methoxy-5-methylthiotriazolium salt (2b) (0.29 g), after flash chromatography (hexane), gave 4,5-bis(methylthio)-2-phenyltriazole (7d) (52 mg, 23%), identical with the material above. The column was then eluted with ethyl acetate–hexane (1 : 4) to give 4-methylthio-2-phenyltriazole (9b) (0.13 g, 73%), described previously.[1]

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (0.20 g), after preparative t.l.c. (dichloromethane–hexane, 1 : 2), gave *4-methyl-5-methylthio-2-phenyl-1,2,3-triazole* (4q) (43 mg, 29%) (R_F 0.47) as a colourless oil; this was dissolved in hexane, filtered through activated carbon, and reprecipitated from hexane (Found: C, 58.4; H, 5.1; N, 20.3. $C_{10}H_{11}N_3S$ requires C, 58.5; H, 5.4; N, 20.45%); *m/e* 205 (100%, M^+); δ ($CDCl_3$) 8.0—7.85 and 7.55—7.1 (2 H, m, and 3 H, m, Ph), 2.55 (3 H, s, SMe), and 2.32 (3 H, s, CMe). The next fraction contained 4-methyl-2-phenyltriazole (9c) (35 mg, 30%), identical with the material described previously.[14]

Reaction with Thioacetate Ions.—(*a*) The 5-chloro-1-methoxytriazolium salt (2a) (69 mg), potassium thioacetate (58 (mg), and acetonitrile (0.7 ml) were stirred together for 3 d. The acetonitrile was then removed and the residue extracted with dichloromethane (4 × 5 ml); the dichloromethane was removed and the residue flash chromatographed (dichloromethane–hexane, 1 : 1) to give several compounds in minor amounts. Then 4-acetylthio-2-phenyltriazole (11f) (10 mg, 11%), described previously,[1] was eluted from the column. Subsequent elution with ethyl acetate–hexane (1 : 4) afforded the 5-chlorotriazole-1-oxide (1a) (27 mg, 60%), described previously.[1]

(*b*) Similarly, the 1-methoxy-5-methylthiotriazolium salt (2b) (33 mg) gave a crude product which, upon preparative t.l.c. (dichloromethane–hexane, 1 : 2), yielded 4-methylthio-2-phenyltriazole (9b) (10 mg, 49%) (R_F 0.28) and the 5-methylthiotriazole 1-oxide (1b) (4 mg, 20%) (R_F 0), both identical with the compounds described previously.[1] In addition, minor amounts of several unidentified compounds were isolated from the plate.

(*c*) Similarly, the 1-methoxy-5-methyltriazolium salt (2c) (25 mg) gave 4-methoxy-5-methyl-2-phenyltriazole (4n) (1 mg, 6%) (R_F 0.55) and 4-methyl-2-phenyltriazole (9c) (9 mg, 65%) (R_F 0.35), both described previously,[1,14] and the 5-methyltriazole 1-oxide (1c) (4 mg, 23%), identical with the material described above.

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