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Reactions Between Azolium Salts and Nucleophilic Reagents

VII. The Preparation and Properties of 1,3-Disubstituted 4-Methylthio-1,2,3-triazolium Salts

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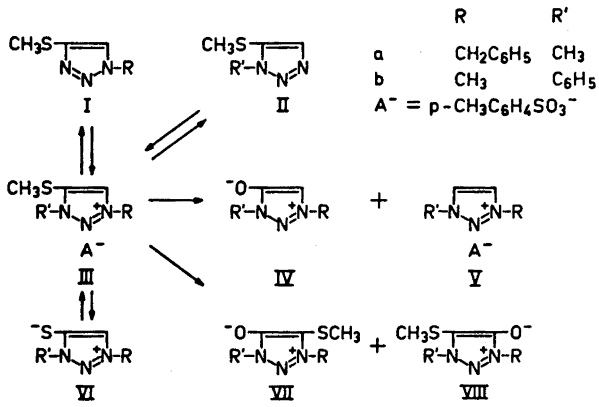
1,3-Disubstituted 4-methylthio-1,2,3-triazolium salts (III) have been prepared from methyl tosylate and either 1-substituted 4-methylthio-1,2,3-triazoles (I), 1-substituted 5-methylthio-1,2,3-triazoles (II), or 1,3-disubstituted 4-(1,2,3-triazolio)sulfides (VI). The methylthio-1,2,3-triazolium salts (III) dealkylate in piperidine giving (1,2,3-triazolio)sulfides (VI). In basic solution nucleophilic displacement of the methylthio group takes place. Concurrently, (III) gives off methylsulfonium ions which may be trapped with methanethiolate ions or transferred to (III) itself providing the dimethylthio compound (XI) and the triazolium salt (V). Similarly, (XI) may thiomethylate (V) and an equilibrium mixture of (III), (IX), (V), and (XII) arises. Finally, the methylthio compounds (III), (XI), and (XII) react with substitution or dealkylation.

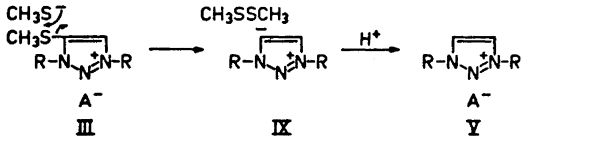
In previous papers [1,2] the nucleophilic substitution of bromo-1,2,3-triazolium salts was studied. It was found that bromo-1,2,3-triazolium salts are bromonium ion donors and that the direct substitution was complicated by competing interbromination reactions. In the hope that this complication might be avoided the reaction of methylthio-1,2,3-triazolium salts (III) with nucleophilic reagents has now been investigated.

1,3-Disubstituted 4-methylthio-1,2,3-triazolium *p*-toluenesulfonates (III) were readily prepared by treatment of 1-substituted 4-methylthio-1,2,3-triazoles (I), 1-substituted 5-methylthio-1,2,3-triazoles (II), or 1,3-disubstituted 4-(1,2,3-triazolio)sulfides (VI) with methyl *p*-toluenesulfonate. Thus 1-phenyl-5-methylthio-1,2,3-triazole (IIb) and methyl tosylate afforded 1-methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) in quantitative yield. Similarly, 1-benzyl-4-methylthio-1,2,3-triazole (Ia) and [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (VIa) both afforded 1-benzyl-3-methyl-4-methylthio-1,2,3-triazolium tosylate (IIIa) in 99 % and 71 % yields, respectively. The preparation of 1-substituted 4-methylthio-1,2,3-triazoles (I) and of the (1,2,3-triazolio)sulfides (VI) will be described in a forthcoming paper.[3]

Scheme 1



Scheme 2



The thermal stability of the methylthio-1,2,3-triazolium salts (III) was first investigated. In contrast to the methoxy-1,2,3-triazolium salts,[4,5] the methylthio-1,2,3-triazolium tosylates (III) are stable, even at elevated temperature. Dealkylation of (III) required prolonged heating with sodium iodide in acetone solution. Thus, 1-methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) afforded 1-phenyl-5-methylthio-1,2,3-triazole (IIb) as the sole product. When treated with piperidine, however, (IIIb) gave [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (VIb) as the major product. In addition, a minor amount of (IIb) was formed. These experiments indicate that (1,2,3-triazolio)sulfides may be prepared from methylthio-1,2,3-triazoles and *vice versa* by appropriate dealkylation of the methylthio-1,2,3-triazolium salts (III).

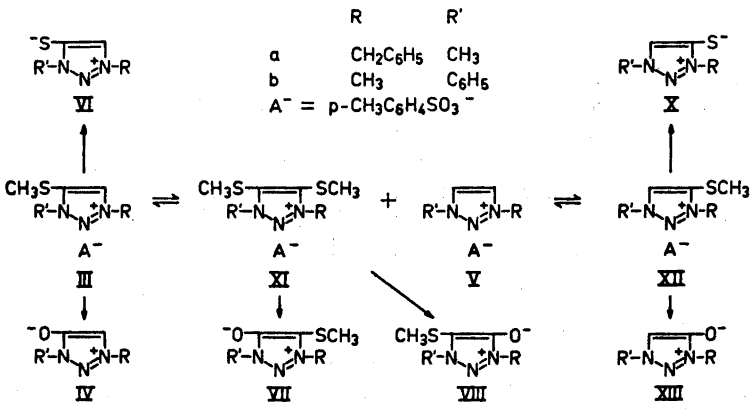
When 1-methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) was heated to reflux with 1 N aqueous sodium hydroxide, it gave a mixture of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]oxide (IVb) (47 %), 1-methyl-3-phenyl-1,2,3-triazolium tosylate (Vb) (30 %), dimethyl disulfide (29 %), [1-methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb) (5 %), and [1-phenyl-3-methyl-5-methylthio-4(1,2,3-triazolio)]oxide (VIIIb) (3 %). This result already shows that the reaction between methylthio-1,2,3-triazolium salts and base is not a simple one.

The [methylphenyl-(1,2,3-triazolio)]oxide (IVb) may be formed from the starting material (IIIb) by nucleophilic displacement of the methylthio group with a hydroxy group followed by deprotonation. The methylphenyltriazolium

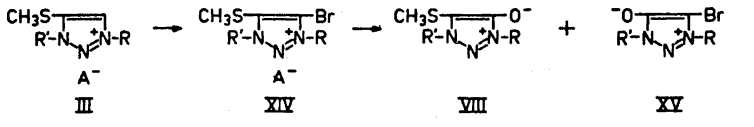
salt (Vb) formally arises by a reduction of the starting material (IIIb). The dimethyl disulfide and the [methylthio-(1,2,3-triazolio)]oxides (VIIb) and (VIIIb) are oxidation products. The only compounds likely to be reducing agents are the starting material (IIIb) and the methanethiolate ion liberated by the competing substitution of (IIIb).* The methylthio-1,2,3-triazolium salt (IIIb) may transfer methylsulfonium ions to suitable acceptors. This reaction seems likely, since the anion thereby formed is relatively stable, as indicated by the deuterium exchange rates of H – 4 in the methylphenyltriazolium salt (Vb.).[1] Protonation of the anion in turn furnishes the methylphenyltriazolium salt (Vb). The reaction resembles the bromonium ion formation from bromo-substituted 1,2,3-triazolium salt in basic solution.[1,6] If methanethiolate ions, liberated by the competing substitution reaction, are the acceptors of the methylsulfonium ions dimethyl disulfide is formed (Scheme 2). In fact, the methylthio-1,2,3-triazolium salt (IIIb) and pure sodium methanethiolate gave the methylphenyltriazolium salt (Vb) and dimethyl disulfide according to this Scheme (see below).

The [methylthio-(1,2,3-triazolio)]oxides (VIIb) and (VIIIb) are presumably formed by nucleophilic displacement of either of the methylthio groups of the di(methylthio)-1,2,3-triazolium salt (XIb). The latter, in turn, may be formed, together with (Vb), by a base catalyzed transfer of a methylsulfonium ion from (IIIb) to the anion of (IIIb) (Scheme 3). This reaction resembles the

Scheme 3



Scheme 4



* The reduction by hydroxide ions is unlikely and (triazolio)oxides such as (IVb) have no reducing or oxidizing properties under the conditions of the reaction.

base catalyzed selfhalogenation of bromo-1,2,3-triazolium salts.[1,6] As in these situations, the di(methylthio)-1,2,3-triazolium salt (XIb) may thiomethylate the methylphenyltriazolium salt (Vb) with formation of the starting material (IIIb) or the isomeric compound (XIIb). In fact, products derived from (XIIb) were isolated in the reaction between the methylthio-1,2,3-triazolium salt (IIIb) and aqueous sodium methanethiolate. The chief products from this reaction were dimethyl disulfide, the methylphenyltriazolium tosylate (Vb), and 1-phenyl-1,2,3-triazole. The latter undoubtedly arises by dequaternization of (Vb). (Vb) and dimethyl disulfide are supposedly formed according to Scheme 2. In addition, the reaction between (IIIb) and sodium methanethiolate gave [1-methyl-3-phenyl-4-(1,2,3-triazolio)]oxide (IVb) and sulfide (VIb) together with [1-phenyl-3-methyl-4-(1,2,3-triazolio)]oxide (XIIIb) and -sulfide (Xb). The oxide (IVb) and the sulfide (VIb) may arise by substitution and *S*-dealkylation of the starting material (IIIb), respectively. Similarly, the oxide (XIIIb) and the sulfide (Xb) may be formed from the methylthio-1,2,3-triazolium salt (XIIb). The latter in its turn may arise *via* interthiomethylations according to Scheme 3. The lack of products derived from the di(methylthio)-1,2,3-triazolium salt (XIb) may be rationalized by assuming that (XIb) thiomethylates (Vb) before substitution or dealkylation occur. Similar results were found in the reaction between bromo-1,2,3-triazolium salts and sodium methoxide.[2,7]

The thiomethylation reactions probably follow an ionic mechanism as described above. Another possibility would be transfer of methylthio radicals. However, the ionic mechanism is preferred since all reactions are base catalyzed and take place in aqueous solution at moderate temperature, even in the dark, and since the addition of hydroquinone did not change the reaction course.

Like the methylthio-1,2,3-triazolium salt (IIIb), 1-benzyl-3-methyl-4-methylthio-1,2,3-triazolium tosylate (IIIa) has thiomethylating properties. Thus (IIIa), when treated with 1 N sodium hydroxide, gave 1-methyl-3-benzyl-1,2,3-triazolium tosylate (Va) (12 %) and dimethyl disulfide according to Scheme 2. In addition, minor amounts of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (VIa) and 1-methyl-5-methylthio-1,2,3-triazole (IIa) were isolated. The latter two compounds probably arise by dealkylation of the starting material. The major product, however, was the substitution product (IVa) (71 %). No [methylthio-1,2,3-triazolio)]oxides (VIIa) or (VIIIa) were isolated. The product distribution indicates, that in the reaction of (IIIa) with sodium hydroxide substitution is more important than thiomethylation.

When monobromo-1,2,3-triazolium salts were treated with methanolic sodium methoxide the rate of substitution became higher than that of selfhalogenation.[2,7] Thus, 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate and sodium methoxide, *via* substitution and *O*-dealkylation afforded [1,3-dimethyl-4-(1,2,3-triazolio)]oxide as the sole product.[7]

In fact, the methylthio-1,2,3-triazolium salt (IIIb), when treated with sodium methoxide, gave the (triazolio)oxide (IVb) as the sole product. This indicates that the substitution rate becomes much higher than the thiomethylation rate when sodium methoxide is used as the nucleophilic reagent.

The [methylthio-(1,2,3-triazolio)]oxide (VIIIb) was prepared independently by reaction of the methylthio-triazolium salt (IIIb) with *N*-bromoacetamide

and base. When 1 N aqueous sodium hydroxide was used as the base, 46 % of (VIIIb) was obatined. The [bromo-(1,2,3-triazolio)]oxide (XVb) was isolated as a byproduct. Like other 1,2,3-triazolium salts,[1,6] (IIIb) is brominated producing (XIVb). The latter, in its turn, by substitution of the bromine atom or of the methylthio group, affords (VIIIb) and (XVb), respectively. When 1 N sodium methoxide was used as the base, (IIIb) and *N*-bromoacetamide furnished (VIIIb) in 60 % yield. The (triazolio)oxide (IVb), formed by substitution of the starting material, was isolated as a byproduct.

In table 2 are presented NMR-data of all compounds prepared. In the 1,2,3-triazole series (and other azoles as well) it may be impossible to distinguish between aromatic $O-CH_3$ and $N-CH_3$ groups on the basis of their δ-values. However, the two types of methyl groups may be identified unambiguously through the $^{13}C-H$ coupling constants.[8] The same method may be used to distinguish between aromatic $C-CH_3$ groups (δ 2.2 – 2.4; $J_{^{13}C-H}$ 130 – 132[1,8]) and $S-CH_3$ groups (δ 2.2 – 2.5; $J_{^{13}C-H}$ 142 – 144 (Table 2 and Ref. 3)).

EXPERIMENTAL

Thin layer and column chromatography were carried out as described previously.[9] NMR-spectra were obtained on a Varian A – 60 instrument. Position of signals are given in ppm (δ-values) relative to TMS, when not otherwise stated. Deuteriochloroform was used as a solvent, unless otherwise stated. Melting points are uncorrected. All products were identified through their melting points, IR-, and NMR-spectra.

Preparation of methylthio-1,2,3-triazolium salts

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb). 1-Phenyl-5-methylthio-1,2,3-triazole (IIb)[10] (3.63 g) and methyl tosylate (3.65 ml) were heated to 100°C for 3 h. The oil formed was extracted with ether (5 × 10 ml) and was reprecipitated three times from methylene chloride-ether yielding 7.25 g (100 %) of 1-methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate(IIIb) as a colourless oil which could not be induced to crystallize. (Found: C 53.93; H 5.16; N 11.32; S 17.05. Calc. for $C_{17}H_{19}N_3O_3S_2$: C 54.08; H 5.08: N 11.13; S 16.99.) NMR-data are given in Table 1.

Table 1. NMR-spectroscopic data and deuterium exchange rates of 4-methylthio-1,2,3-triazolium tosylates.[a]

Compound	NMR H-5 ppm	*N*-CH_3 ppm	*N*-CH_2 ppm	*S*-CH_3 ppm	Exchange rate of H_5[b] pD	$T_{\frac{1}{2}}$ min	Relative rate[c]
1-Benzyl-3-methyl-4-methylthio-triazolium tosylate (IIIa)	8.48	4.14	5.75	2.58	9.86	2.4	5.5
1-Methyl-3-phenyl-4-methylthio-triazolium tosylate (IIIb)	8.64	4.45		2.65	7.96	32.5	30

[a] NMR-spectra were obtained in deuterium oxide with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.
[b] The exchange rates were determined as described previously.[1]
[c] The rates relative to the exchange rate of 1,3-dimethyl-1,2,3-triazolium tosylate.[1]

1-Benzyl-3-methyl-4-methylthio-1,2,3-triazolium tosylate (IIIa). *A.* 1-Benzyl-4-methylthio-1,2,3-triazole (Ia)[3] (101 mg) and methyl tosylate (0.92 ml) were heated to 100°C for 3 h. The product was washed with ether (5 × 10 ml), and recrystallized from methylene chloride-ether; this gave 191 mg (99 %) of 1-benzyl-3-methyl-4-methylthio-1,2,3-triazolium tosylate (IIIa) as colourless crystals, m.p. 150–151°C. (Found: C. 55.32; H 5.35; N 10.87; S 16.32. Calc. for $C_{18}H_{21}N_3O_3S_2$: C 55.22; H 5.41; N 10.73; S 16.38.)

B. Similarly, [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (VIa)[3] (863 mg) and methyl tosylate (0.84 ml) gave, after heating, ether washing, recrystallization, and washing with ethyl acetate, 1.21 g (71 %) of (IIIa). The product was identical with the compound described above.

Dealkylation of the methylthio-1,2,3-triazolium salt (IIIb)

A. 1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) (104 mg) and chloroform (2.00 ml) were heated in a sealed tube for 140°C for 5 h. Removal of the chloroform afforded the unchanged starting material in quantitative yield.

B. (IIIb) (155 mg), sodium iodide (123 mg), and dry acetone (5.00 ml) were heated to 180°C for 3 h. Removal of the acetone left a brown oil which contained only traces of the (triazolio)sulfide (VIb) as shown by NMR and TLC. The oil was chromatographed on silica gel (20 g) using ether as eluent. The first fraction was not identified further. The next fraction contained 40 mg (51 %) of 1-phenyl-5-methylthio-1,2,3-triazole (IIb) as a yellow oil. The material was identical with that described previously.[10]

C. (IIIb) (455 mg) and piperidine (6.00 ml) were heated to reflux for 3 h. The piperidine was then removed *in vacuo* at 30°C. The residue was dissolved in water (30 ml) and was extracted with methylene chloride (4 × 10 ml). The methylene chloride solution was dried and the solvent was removed giving 270 mg of a yellow oil which was chromatographed on silica gel (10 g) using ethyl acetate as eluent. The first fraction contained 65 mg (28 %) of 1-phenyl-5-methylthio-1,2,3-triazole (IIb) as a yellow oil. The column was then eluted with ethyl acetate methanol (1:1). This gave 159 mg (69 %) of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (VIb) as a yellow oil which crystallized on standing for 1 day, m.p. 99–101°C. Recrystallization from chloroform-ether raised the melting point to 112°C. (Found: C 56.58; H 4.93; N 22.04; S 16.70. Calc. for $C_9H_9N_3S$: C 56.53; H 4.75; N 21.98; S 16.78.) The compound was identified through its NMR-spectrum (Table 2) which showed an N-CH_3 signal. Furthermore, it was identical with the material described in a forthcoming paper.[3]

Reaction with nucleophilic reagents

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) and sodium hydroxide. (IIIb) (465 mg) and 1 N sodium hydroxide (2.50 ml) were heated to 100°C for 3 h. The water was then removed *in vacuo* and the residue was extracted with boiling chloroform (5 × 10 ml). The chloroform was evaporated and the residue thus obtained was extracted with ethyl acetate (4 × 10 ml). The ethyl acetate insoluble material consisted of 124 mg (30 %) of 1-methyl-3-phenyl-1,2,3-triazolium tosylate (Vb) as yellow crystals, m.p. 114–115°C. The compound was identical with the material described previously.[1] The ethyl acetate extract contained a brown oil which was chromatographed on silica gel (20 g) using ethyl acetate as eluent. The first fraction contained a minor amount of an unidentified compound. The next fraction contained (14 mg) (5 %) of [1-methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb) as a yellow oil which could not be induced to crystallize. Reprecipitation from ethyl acetate-ether gave the pure compound. (Found: C 54.54; H 5.09; N 18.84. Calc. for $C_{10}H_{11}N_3OS$: C 54.28; H 5.01; N 18.99.) The IR-spectrum showed an absorption at 1642 cm^{-1}, characteristic of (triazolio)oxides.[4] The NMR-spectrum showed an N-CH_3 and an S-CH_3 signal (Table 2). The column was then eluted with ethyl acetate-methanol (1:1). This gave 9 mg (3 %) of [1-phenyl-3-methyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIIb) as a yellow oil, identical with the material prepared below. The next fraction contained 101 mg (47 %) of [1-methyl-3-phenyl-4-

Table 2. Spectroscopic data of 4-(1,2,3-triazolio)oxides and sulfides.

Compound	Infrared [a] cm^{-1}	NMR [b] H-5 ppm	N-CH_3 ppm	$J_{^{13}C-H}$ Hz	S-CH_3 ppm	$J_{^{13}C-H}$ Hz
[1-Methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb)	1642		4.05	144	2.37	142
[1-Phenyl-3-methyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIIb)	1655		3.84	145	2.28	144
[1-Methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (VIb)		7.70	4.11	145		
[1-Phenyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Xb)		8.08	4.18	144		

[a] IR-spectra were obtained in potassium bromide discs.
[b] NMR-spectra were obtained in deuteriochloroform with tetramethylsilane (TMS) as internal standard.

(1,2,3-triazolio)]oxide (IVb) as yellow crystals, m.p. 86 – 92°C. Recrystallization from ethyl acetate-hexane raised the melting point to 99 – 100°C. The compound was identical with the material described previously.[4]

A separate experiment was carried out in which (IIIb) was heated with 1 N sodium hydroxide to 100°C for 3 h in a sealed tube. The reaction mixture was then extracted with a known amount of deuteriochloroform containing a known amount of methylene chloride. The chloroform extract showed an NMR-signal af δ 2.44 due to dimethyl disulfide. The signal was identified by adding the authentic substance to the solution. Using the methylene chloride peak as an integration standard the yield of dimethyl disulfide was determined to 29 %. Methanethiole and methanethiolate ions were present in the chloroform and the water phase, respectively. The compounds were identified through NMR-spectroscopy by adding the authentic substances to the solutions.

With 0.35 mol-equiv. of hydroquinone added, the reaction between (IIIb) and 1 N sodium hydroxide analogously gave a chloroform extract which, as shown through the NMR-spectrum, contained all the compounds formed when hydroquinone was not present. Moreover, the ratios between the products were almost the same. Working up as above gave the [methylthio-(1,2,3-triazolio)]oxides (VIIb) and (VIIIb) in 3 and 1 % yield, respectively. The (triazolio)oxide (IVb) was isolated in 36 % yield.

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) and sodium methoxide. (IIIb) (1.65 g) and sodium methoxide (8.90 ml) were heated to reflux for 3 h and the mixture was worked up as in the preceeding experiment. There was no residue from the latter extraction. The ethyl acetate extract was filtered through activated carbon. Removal of the ethyl acetate afforded 647 mg (84 %) of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]oxide (IVb), m.p. 87 – 93°C. Recrystallization from ethyl acetate-hexane raised the melting point to 98 – 100°C. The material was identical with that described previously.[4]

1-Benzyl-3-methyl-4-methylthio-1,2,3-triazolium tosylate (IIIa) and sodium hydroxide. (IIIa) (592 mg) and 1 N sodium hydroxide (3.10 ml) were heated to reflux for 8 h and the mixture was worked up as in the preceeding experiment. The residue from the ethyl acetate extraction contained 77 mg of 4. 4:1 mixture of 1-methyl-3-benzyl-1,2,3-triazolium tosylate (Va) and the starting material (IIIa) corresponding to 12 and 3 % yield, respectively. The compounds were identified through NMR-spectroscopy by adding the authentic substances to the solution.

The ethyl acetate extract contained a yellow oil which was chromatographed on silica gel (22 g) using ethyl acetate as eluent. The first fraction contained 11 mg (6 %) of

1-methyl-5-methylthio-1,2,3-triazole (IIa) as a yellow oil, identical with the material described elsewhere.[3] The next fraction contained 30 mg (10 %) of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (VIa) as colourless crystals, m.p. 128–129°C. The compound was identical with the material described elsewhere.[3] The column was then eluted with ethyl acetate-methanol (1:1). This gave 204 mg (71 %) of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]oxide (IVa) as colourless crystals, m.p. 87–90°C. The compound was identical with the material described previously.[8] Dimethyl disulfide was identified in a separate experiment as described above.

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb) and sodium methanethiolate. (IIIb) (468 mg), sodium methanethiolate[11] (freshly prepared) (270 mg), and water (1.12 ml) were heated to 100°C for 3 h. The solvent was then removed *in vacuo* and the residue was extracted with boiling chloroform (5 × 10 ml) and ethyl acetate (4 × 10 ml) as described in the reaction of (IIIb) with sodium hydroxide. The residue from the latter extraction consisted of 101 mg (25 %) of 1-methyl-3-phenyl-1,2,3-triazolium tosylate (Vb), colourless crystals, m.p. 103–107°C. Recrystallization from methanol-ether raised the melting point to 113–114°C. The compound was identical with the material described previously.[1] The ethyl acetate-extract contained an oil which was chromatographed on silica gel (30 g) using ethyl acetate as eluent. The first fraction contained 45 mg (25 %) of 1-phenyl-1,2,3-triazole as yellow crystals, m.p. 45–48°C. Recrystallization from water raised the melting point to 52–53°C. The compound was identical with an authentic sample.[12] The next fraction contained 46 mg (17 %) of [1-phenyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Xb) as cream coloured crystals, m.p. 193–194°C. Recrystallization from chloroform-ether did not raise the melting point. (Found: C 56.66; H 4.78; N 21.83; S 16.71. Calc. for $C_9H_9N_3S$: C 56.53; H 4.75; N 21.98; S 16.78.) The compound was identified through its NMR-spectrum which showed an $N-CH_3$ signal (Table 2). The next fraction contained 8 mg (3 %) of [1-methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb) identical with the material described above. The column was then eluted with ethyl acetate-methanol (1:1). This gave 29 mg (12 %) of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (VIb) as a yellow oil. Crystallization from chloroform-ether gave colourless crystals, m.p. 110°C. The compound was identical with the material described below. The next fraction contained 14 mg of a mixture of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]oxide (IVb) (4.6 %) and [1-phenyl-3-methyl-4-(1,2,3-triazolio)]oxide (XIIIb) (1.7 %) as indicated by NMR-spectra. The two compounds were identified by addition of the authentic substances to the solution.[1,4] Dimethyl disulfide was identified, as described above, in a separate experiment which was carried out in a sealed tube. The yield of dimethyl disulfide was 72 %.

Reaction with *N*-bromoacetamide

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb), N-bromoacetamide, and sodium hydroxide. (IIIb) (657 mg), *N*-bromoacetamide (288 mg), and 1 N sodium hydroxide (9.70 ml) were kept at room temperature for 14 days. The solvent was then removed *in vacuo* and the residue was extracted with boiling chloroform (5 × 10 ml). Removal of the chloroform left an orange oil (511 mg) which was chromatographed on silica gel (10 g) using ethyl acetate as eluent. The first fraction contained a mixture which was purified by preparative thin layer chromatography (one 40 cm plate with a 1 mm layer of silica gel) eluting four times with chloroform-acetone-hexane (12:3:5). The first fraction contained 11.6 mg (3 %) of [1-methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb) as an oil identical with the material described above. (VIIb) is probably formed by reaction of the starting material with hydroxide ions according to Scheme 3. The next fraction contained 65 mg (15 %) of [1-methyl-3-phenyl-5-bromo-4-(1,2,3-triazolio)]oxide (XVb) as an oil which crystallized on standing, m.p. 82–86°C. Recrystallization from ethyl acetate-ether raised the melting point to 106–108°C. The compound was identical with the material described previously.[1] The next fraction contained 178 mg (46 %) of [1-phenyl-3-methyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIIb) as a colourless oil which crystallized on standing, m.p. 106–109°C. The material was purified by extraction with boiling ether (10 × 10 ml). The volume of the combined extracts was reduced to *ca.* 10 ml and the solution was cooled to −30°C. Filtration

afforded the pure material, m.p. 112°C. (Found: C 54.43; H 5.06; N 18.87; S 14.51. Calc. for $C_{10}H_{11}N_3OS$: C 54.28; H 5.01; N 18.99; S 14.49.)

1-Methyl-3-phenyl-4-methylthio-1,2,3-triazolium tosylate (IIIb), N-bromoacetamide, and sodium methoxide. (IIIb) (700 mg), *N*-bromoacetamide (308 mg), and 1 N sodium methoxide (10.30 ml) were kept at room temperature for 14 days. The solvent was then removed and the residue was extracted with boiling chloroform (5 × 10 ml). Removal of the chloroform left an orange oil (444 mg) which was chromatographed on silica gel (30 g) using ethyl acetate as eluent. The first fraction contained 15 mg (6 %) of 1-phenyl-1,2,3-triazole as a yellow oil which crystallized on standing. The identity was proved by IR- and NMR-spectra. The next fraction contained 16 mg (4 %) of [1-methyl-3-phenyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIb) as a yellow oil, identical with the material described above. The column was then eluted with ethyl acetate-methanol (1:1). This gave 246 mg (60 %) of [1-phenyl-3-methyl-5-methylthio-4-(1,2,3-triazolio)]oxide (VIIIb) as an oil which crystallized on standing, m.p. 101 – 109°C. Purification as described above raised the melting point to 112°C. The compound was identical with the material described above. The next fraction contained 97 mg (30 %) of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]oxide (IVb) as colourless crystals, m.p. 91 – 99°C. Recrystallization from ethyl acetate-hexane with cooling in dry ice raised the melting point to 95 – 99°C. The compound was identical with the material described previously.[1]

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