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Reactions Between Azolium Salts and Nucleophilic Reagents

VIII. The Preparation and Properties of 1,3-Disubstituted 4-(1,2,3-Triazolio)sulfides

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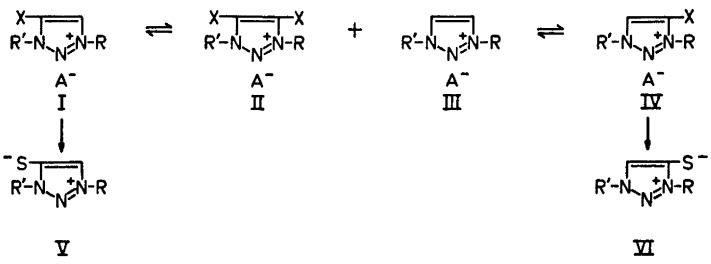
1,3-Disubstituted-monohalo-1,2,3-triazolium salts (I) when treated with sodium sulfide in dimethylformamide produce 1,3-disubstituted 4-(1,2,3-triazolio)sulfides (V). In addition, interhalogenation of I gives a mixture of I with the dibromo compound II, the unsubstituted salt III, and the monobromo compound IV. IV affords the 4-(1,2,3-triazolio)sulfide (VI), whereas II decomposes. The 4-(1,2,3-triazolio) sulfides, when heated in an organic solvent, produce alkylthio-1,2,3-triazoles, probably by bimolecular interalkylation. Benzoylation of 4-(1,2,3-triazolio)sulfides gives 1-substituted-4-benzoylthio-1,2,3-triazoles (XI) and/or 1-substituted 5-benzoylthio-1,2,3-triazoles (XIV) *via* the salt XIII. The relative tendencies of various alkyl groups to undergo detachment in these reactions are discussed. The benzoylthio-1,2,3-triazoles (XI and XIV) by hydrolysis produce the mercapto-1,2,3-triazoles (XII and XV), respectively. Methylation of these gives *S*-methyl derivatives, exclusively. The 4-(1,2,3-triazolio)sulfide (Vb), when treated with bromine affords the sulfenyl bromide XVIIb. The latter reacts with acetone and cyclohexene in the manner characteristic of other sulfenyl bromides.

The properties of 4-(1,2,3-triazolio)sulfides and -oxides are compared and discussed.

In continuation of the investigation of the reaction between azolium salts and nucleophilic reagents 1,3-disubstituted 4-halo-1,2,3-triazolium salts (I) have been treated with sulfide ions in order to prepare the mesoionic 4-(1,2,3-triazolio)sulfides (V). This reaction has been dealt with in a preliminary communication,[1] but is described here in detail. The 4-(1,2,3-triazolio)sulfides were prepared with a view to study their properties with special reference to a comparison with the properties of the 4-(1,2,3-triazolio)oxides described in previous papers.[2,3]

It was found that treatment of 1,3-disubstituted 4-halo-1,2,3-triazolium salts (I) with sodium sulfide in dimethylformamide furnished 1,3-disubstituted

Scheme 1



	R	R'	X
a	CH_3	CH_3	Br
b	$CH_2C_6H_5$	CH_3	Br
c	CH_3	$CH_2C_6H_5$	Br
d	CH_3	C_6H_5	Cl

$A^- = p\text{-}CH_3C_6H_4SO_3^-$

4-(1,2,3-triazolio)sulfides (V) by nucleophilic displacement of halogen.[1] Thus, 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (Ia) afforded [1,3-dimethyl-4-(1,2,3-triazolio)]sulfide in 55 % yield. As a byproduct, 1,3-dimethyl-1,2,3-triazolium tosylate (IIIa) (23 %) was isolated.

Similarly, 1-benzyl-3-methyl-4-bromo-1,2,3-triazolium tosylate (Ib) gave a mixture of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) and 1-methyl-3-benzyl-1,2,3-triazolium tosylate (IIIb). In addition, the isomeric 4-(1,2,3-triazolio)sulfide (VIb) was isolated. A separate experiment showed that no changes took place when the 4-(1,2,3-triazolio)sulfide (Vb) was subjected to the conditions of the reaction. Conversion of Vb to VIb is therefore excluded. Most probably, VIb is formed by substitution of the bromo compound IVb. The latter undoubtedly arises through the previously described [4,5] equilibrium between the two monobromo compounds I and IV and a mixture of the dibromo compound II and the unsubstituted derivative III. This also explains the isolation of the triazolium salts IIIa and IIIb from Ia and Ib, respectively. If the above mentioned equilibrium is present it would be expected that some of the dibromo compound II should also be formed. However, neither II, nor substitution products derived therefrom could be detected. This is probably due to the fact that the dibromo compound II decomposes during the reaction as seen from separate experiments in which the pure dibromo compounds IIa and IIb were treated with sodium sulfide in dimethyl formamide. This gave a complex mixture of decomposition products and similar mixtures were found as byproducts from the reactions of the monobromo compounds Ia and Ib with sulfide ions.

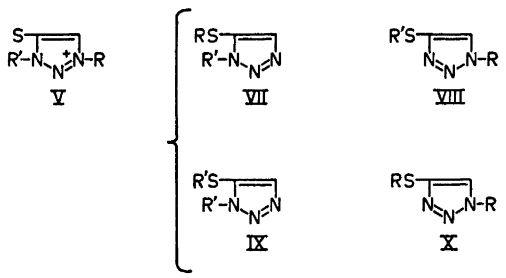
1-Methyl-3-benzyl-4-bromo-1,2,3-triazolium tosylate (IVb) reacted in the same manner with sulfide ions yielding [1-methyl-3-benzyl-4-(1,2,3-triazolio)]-sulfide (VIb) as the chief product. Again, the isomeric 4-(1,2,3-triazolio)sulfide (Vb) and 1-methyl-3-benzyl-1,2,3-triazolium tosylate (IIIb) were isolated as

byproducts, indicating that interhalogenation of the starting material has taken place.

It has been found that when chloro-1,2,3-triazolium salts are treated with aqueous sodium hydroxide, no interhalogenation takes place.[6] This is in agreement with the fact that chloronium ions are less stable than bromonium ions. A similar result was found by using the present reaction, since 1-methyl-3-phenyl-4-chloro-1,2,3-triazolium tosylate (Id) afforded [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd) in almost quantitative yield by treatment with sulfide ions.

Heating of 4-(1,2,3-triazolio)sulfides in an organic solvent at 180°C results in transfer of alkyl groups with the formation of alkylthio-1,2,3-triazoles.[1] Thus, [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd) rearranged slowly producing 1-phenyl-5-methylthio-1,2,3-triazole (VIId). 4-(1,2,3-Triazolio)sulfides with an *N*-alkyl group adjacent to the sulfur atom were apparently

Scheme 2



rearranged more readily. Thus, [1,3-dimethyl-4-(1,2,3-triazolio)]sulfide (Va) gave the two possible rearrangement products VIIa and VIIIa; [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) gave three of the four possible products; and [1-methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (VIb) afforded all of the four possible products (Scheme 2 and Table 1). The structures of the alkylthio-1,2,3-triazoles were proved as follows. The structure of 1-benzyl-4-methylthio-1,2,3-triazole (VIIIb) is given by its formation in the methylation of 1-benzyl-4-mercapto-1,2,3-triazole (XIIb) (see below). The other isomer is therefore undoubtedly 1-benzyl-5-methylthio-1,2,3-triazole (VIIc). A comparison of the NMR-spectra of VIIIb and VIIc indicates that the *S*-alkyl protons of the 1,5-disubstituted compound resonate at a higher field than those of the 1,4-disubstituted isomer. In contrast, the heteroaromatic proton of VIIIb absorbs at a higher field than that of VIIc.* Using these NMR-characteristics the structure of the remaining 6 alkylthio-1,2,3-triazoles, which form three pairs of 1,4- and 1,5-disubstituted isomers, can now be assigned.

Intramolecular alkyl group transfer seems unlikely and cannot account for the formation of the dimethyl- and the dibenzyl-derivatives in the rearrange-

* The *N*-alkyl protons of VIIIb and VIIc resonate at almost the same field. Therefore, the *N*-alkyl-signals cannot be used to make a dinstinction between 1,4- and 1,5-disubstituted isomers VIII and VII, respectively.

Table 1. Products obtained by transalkylation of 4-(1,2,3-triazolio)sulfides.

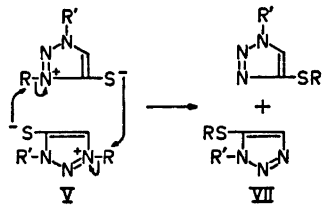
Starting material	Product(s)	Yield %		The nitrogen which donated the *S*-alkyl group
[1-Methyl-3-phenyl-4-(triazolio)]sulfide (Vd)	1-Phenyl-5-methylthio-triazole (VIId)	100		*N*-1
[1,3-Dimethyl-4-(triazolio)] sulfide (Va)	1-Methyl-5-methylthio-triazole (VIIa)	62		*N*-1
	1-Methyl-4-methylthio-triazole (VIIIa)	38		*N*-3
[1-Benzyl-3-methyl-4-(triazolio)]sulfide (Vb)	1-Methyl-5-benzylthio-triazole (VIIb)	82	84	*N*-1
	1-Benzyl-4-benzylthio-triazole (Xb)	2[a]		*N*-1
	1-Methyl-5-methylthio-triazole (VIIa)	13[a]		*N*-3
[1-Methyl-3-benzyl-4-(triazolio)]sulfide (VIb)	1-Benzyl-5-methylthio-triazole (VIIc)	10	30	*N*-1
	1-Methyl-4-methylthio-triazole (VIIIa)	20		*N*-1
	1-Methyl-4-benzylthio-triazole (VIIIc)	43	61	*N*-3
	1-Benzyl-5-benzylthio-triazole (IXc)	18		*N*-3

[a] The yields of Xb and VIIa are expected to be identical. In fact an NMR-spectrum of the crude product mixture indicated the yields of Xb and VIIa to be 9 % and 9 %, respectively.

ment of Vb and VIb. This is further confirmed by the fact that a 1:1 mixture of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) and [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd), when heated in benzene solution, gave, among other products, 1-phenyl-5-benzylthio-1,2,3-triazole (VII; $R' = C_6H_5$, $R = CH_2C_6H_5$).

A bimolecular mechanism appears more likely: An *N*-alkyl group is transferred from one molecule of 4-(1,2,3-triazolio)sulfide to the sulfur atom of another molecule. The second molecule then contributes an *N*-alkyl group to the sulfur atom of the first molecule (Scheme 3).

Scheme 3



V VII

In order to decide whether this type of trans-alkylation is kinetically or thermodynamically determined 1-methyl-4-benzylthio-1,2,3-triazole (VIIIc) was subjected to the trans-alkylation conditions. A thermodynamically controlled reaction should give a mixture of VIIIc with VIIc, VIIIa and IXc (Table 1). However, the material was recovered unchanged indicating kinetic control in the reaction. Consequently, the product distributions reflect the relative aptitude for group detachment. The results summarized in Table 1 indicate that a benzyl group at position 1 is the most labile. Then follows: A benzyl group at position 3, a methyl group at position 1, and, finally, a methyl group at position 3. In methoxy-,[5] benzoyloxy-,[3] and benzoylthio-1, 2, 3-triazolium salts (see below) alkyl groups at position 3 are, on the other hand, more labile than those at position 1.

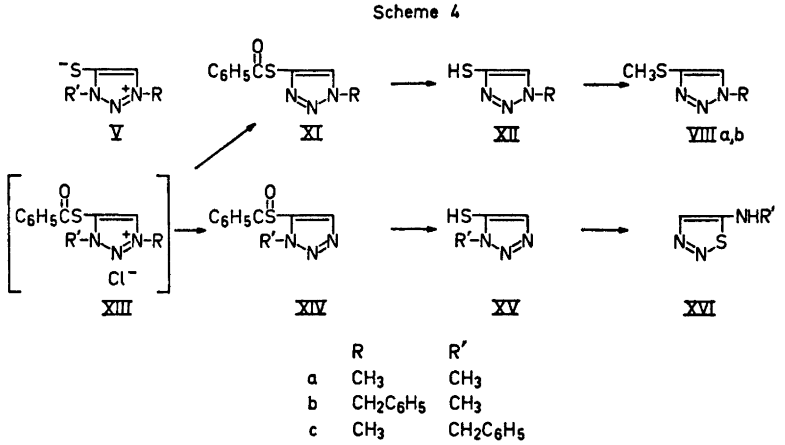
The above results indicate that 4-(1,2,3-triazolio)sulfides have alkylating properties and that they are also readily alkylated. In contrast, 4-(1,2,3-triazolio)oxides are thermally stable and no changes take place when they are heated in benzene at 180°C. The higher reactivity of the 4-(1,2,3-triazolio)-sulfides (V) may be due to a higher charge polarization – or polarizability – in the 4-(1,2,3-triazolio)sulfides than in the corresponding oxides.

The alkylation properties of the 4-(1,2,3-triazolio)sulfides (V) were further demonstrated by the fact that [1-benzyl-4-methyl-4-(1,2,3-triazolio)]sulfide (Vb), when heated with methanolic sodium methoxide, lost its benzyl group to give the anion of 1-methyl-5-mercapto-1,2,3-triazole (XVa). 4-(1,2,3-Triazolio)oxides do not undergo changes under similar conditions. When the solution containing the anion of (XVa) was acidified the mercapto-1,2,3-triazole (XVa) was liberated. Since, however, 1-substituted 5-mercapto-1,2,3-triazoles rearrange readily to 1,2,3-thiadiazoles (see below), alkylation of the anion was preferred. Thus treatment of the anion of (XVa) with methyl iodide afforded 1-methyl-5-methylthio-1,2,3-triazole (VIIa). Similarly, [1-methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (Vc), when heated with sodium methoxide, lost its methyl group yielding the anion of 1-benzyl-5-mercapto-1,2,3-triazole (XVc). The structure of the latter was proved by treatment with methyl iodide to give 1-benzyl-5-methylthio-1,2,3-triazole (VIIc).

The ready alkylation of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) with methyl tosylate to give a methylthio-1,2,3-triazolium tosylate has been described previously.[7] The methylthio-1,2,3-triazolium tosylates thus formed are much more stable than the methoxy-1,2,3-triazolium tosylates formed by treatment of 4-(1,2,3-triazolio)oxides with methyl tosylate.[8]

It was also found that 4-(1,2,3-triazolio)sulfides could be readily acylated when treated with benzoyl chloride.[1] The 1,3-disubstituted 4-benzoylthio-1,2,3-triazolium chlorides (XIII), initially formed, are not stable, but dealkylate under the conditions of the reaction producing 1-substituted-4-benzoylthio-1,2,3-triazoles (XI) and/or 1-substituted 5-benzoylthio-1,2,3-triazoles (XIV). The yields are considerably improved if pyridine is added. Presumably, the pyridine accelerates the reaction by taking up the alkyl chloride, which is cleaved off by the subsequent dealkylation of the intermediate XIII. Provided that equilibrium does not take place under the reaction conditions, the observed product distribution reflects the relative aptitude for alkyl group detachment. The results summarized in Table 2 indicate that a benzyl group at

Scheme 4



	R	R′
a	CH_3	CH_3
b	$CH_2C_6H_5$	CH_3
c	CH_3	$CH_2C_6H_5$

position 3 is the most labile. Then follows: A benzyl group at position 1, a methyl group at position 3, and finally, a methyl group at position 1. These results are similar to those obtained for 1,3-disubstituted 4-benzoyloxy-1,2,3-triazolium salts.[3] However, larger differences in the detachments of 1- and 3-alkyl groups were found in the latter series.

Alkaline hydrolysis of the benzoylthio-1,2,3-triazoles (XI or XIV) gives 1-substituted-4-mercapto-1,2,3-triazoles (XII) and 1-substituted-5-mercapto-1,2,3-triazoles (XV), respectively. The former type of compound is stable when heated with acid. In contrast, 1-methyl-5-mercapto-1,2,3-triazole (XVa) rearranges to 5-methylamino-1,2,3-thiadiazole (XVIa) when treated with hydrochlorid acid. Therefore, the mercapto compound XVa is best liberated with acetic acid after the hydrolysis. Even then, the yield of XVa is only 29 %. Acidification with hydrochloric acid, after the isolation of XVa, gives rise to an additional 71 % of the thiadiazole XVIa. The rearrangement of XVa to

Table 2. Products obtained by reaction of 4-(1,2,3-triazolio)sulfides and benzoyl chloride.

Starting material	Product(s)	Yield %	Leaving group
[1,3-Dimethyl-4- -(triazolio)]sulfide (Va)	1-Methyl-5-benzoylthio- triazole (XIVa)	18	*N*-1
	1-Methyl-4-benzoylthio- triazole (XIa)	57	*N*-3
[1-Benzyl-3-methyl- -(triazolio)]sulfide (Vb)	1-Methyl-5-benzoylthio- triazole (XIVa)	49	*N*-1
	1-Benzyl-4-benzoylthio- triazole (XIb)	32	*N*-3
[1-Methyl-3-benzyl- (triazolio)]sulfide (Vc)	1-Methyl-4-benzoylthio- triazole (XIa)	63	*N*-3

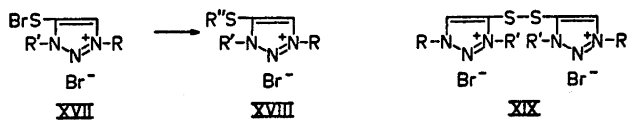
XVIa is in agreement with the well known rearrangement of 1-aryl-5-mercapto-1,2,3-triazoles to 5-anilino-1,2,3-thiadiazoles.[9–11] A related rearrangement is the conversion of 4-mercapto-1,2,3,5,7-pentaazaindenes to 4-amino-1-thia-2,3,5,7-tetraazaindenes.[12–14]

The rearrangement of these mercapto-1,2,3-triazoles to substituted amino-1,2,3-thiadiazoles probably takes place *via* ringclosure of an initially formed diazothioacetanilide,[9–11] the first step being similar to the acid catalyzed formation of diazoacetamides from 1-substituted 5-hydroxy-1,2,3-triazoles.[15–17] In the latter case, 1-aryl derivatives rearrange more readily than 1-alkyl derivatives.[15–16] Consequently, 1-alkyl-5-mercapto-1,2,3-triazoles are expected to rearrange more slowly than 1-aryl-5-mercapto-1,2,3-triazoles. This was confirmed by the fact that pure 1-methyl-5-mercapto-1,2,3-triazole (XVa) did not rearrange, even by prolonged heating with glacial acetic acid, whereas 1-aryl-5-mercapto-1,2,3-triazoles are readily converted under these conditions.[9–11] The arrangement was shown to be reversible, since heating of the 5-methylamino-1,2,3-thiadiazole (XVIa) with 1 N sodium hydroxide followed by acidification with acetic acid gave 1-methyl-5-mercapto-1,2,3-triazole (XVa). The mercapto-1,2,3-triazole (XVa) is a relatively strong acid (pK_a = 8.3), the methylamino-1,2,3-thiadiazole (XVIa) is a relatively strong base and its hydrochloride could be isolated from aqueous solution.

Treatment of 1-benzyl-4-mercapto-1,2,3-triazole (XIIb) with methyliodide afforded the 1-benzyl-4-methylthio-1,2,3-triazole (VIIIb) as the sole product. 1-Methyl-5-mercapto-1,2,3-triazole (XVa), too, gave only the *S*-methylated derivative VIIa. The same was found in the methylation of 1-phenyl-5-mercapto-1,2,3-triazole (XVd).[9] This suggests, that methylation of mercapto-1,2,3-triazoles generally gives *S*-methylated derivatives, exclusively, in contrast to the hydroxy-1,2,3-triazoles which normally give mainly *N*-methylated products.[5,8]

1,3-Disubstituted 4-(1,2,3-triazolio)oxides are readily brominated when treated with bromine in chloroform solution.[2,3] When [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) was subjected to these conditions 1 mol of bromine was consumed. An NMR-spectrum of the product obtained showed a low field heteroaromatic proton signal indicating that substitution has not taken place. Consequently, the product is either a complex between the 4-(1,2,3-triazolio)sulfide (Vb) and bromine, or a sulfur bromine bond has been established with formation of a sulfenyl bromide (XVIIb). A sulfenyl bromide (XVIIb) is expected to react with acetone with formation of 1-benzyl-3-methyl-4-acetylmethylthio-1,2,3-triazolium bromide (XVIIIb, R″ = CH_2COCH_3).[19,20] In fact, the reaction with acetone afforded a compound, the NMR-spectrum of which was in keeping with this structure.

Scheme 5



XVII XVIII XIX

Furthermore, a sulfenyl bromide (XVIIb) is expected to react with cyclohexene with formation of 1-benzyl-3-methyl-4-(2-bromocyclohexylthio)-1,2,3-triazolium bromide (XVIIIb, R″ = 2-bromocyclohexyl).[19,20] Again, the NMR-spectrum of the compound actually formed in the reaction with cyclohexene corresponded to this structure. Finally, a sulfenyl bromide (XVIIb) is expected to react with thiols or thiolates with formation of a disulfide.[19,20] In fact, the reaction with [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) afforded a product the NMR-spectrum of which agreed with the di[1-benzyl-3-methyl-4-(1,2,3-triazolium)]disulfide dibromide (XIXb).

All these experiments indicate that the product formed in the reaction between [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) and bromine is the 1-benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide (XVIIb). When the bromine atom is attached to the sulfur atom the 1,2,3-triazole ring becomes more positively charged and this deactivates the ring towards electrophilic attack. This explains the lack of further attack of bromine in position of 5 XVIIb.*

The initial attack of bromine on the *S*-atom of Vb, instead of attack at position 5, again demonstrates the high nucleophilicity of the sulfur atom of 4-(1,2,3-triazolio)sulfides (V) as compared to the nucleophilicity of the oxygen atom of 4-(1,2,3-triazolio)oxides.

EXPERIMENTAL

Column chromatography was carried out as described previously.[22] Preparative thin layer chromatography (TLC) was carried out on 20 × 40 cm plates with a 1 mm layer of silica gel (Merck, PF_{254}). NMR-spectra were obtained on a Varian A-60 instrument. Position of signals are given in ppm (δ-values) relative to tetramethylsilane (TMS), when not otherwise stated. Deuteriochloroform was used as solvent unless otherwise stated. Melting points are uncorrected. All compounds were identified through their melting point, IR-, and NMR-spectra.

1-Methyl-3-phenyl-4-chloro-1,2,3-triazolium tosylate (Id). 1-Phenyl-5-chloro-1,2,3-triazole [23,24] (1.31 g) and methyl tosylate (1.35 ml) were heated to 100°C for 3 h. The mixture was washed with ether (5 × 10 ml), reprecipitated from methanol-ether, dissolved in water and filtered through activated carbon. Removal of the water and one further reprecipitation from methanol-ether furnished 2.39 g (86 %) of pure 1-methyl-3-phenyl-4-chloro-1,2,3-triazolium tosylate (Id) as a colourless oil which could not be induced to crystallize. (Found: C 52.28; H 4.38; N 11.39; S 8.93; Cl 9.84. Calc. for $C_{16}H_{16}N_3O_3SCl$: C 52.53; H 4.41; N 11.49; S 8.77; Cl 9.69.)

Preparation of 4-(1,2,3-triazolio)sulfides

[1,3-Dimethyl-4-(1,2,3-triazolio)]sulfide (Va). 1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (Ia)[21] (875 mg), sodium sulfide (60 %, Fluka) (329 mg), and dimethylformamide (2.60 ml) were heated with stirring to 100°C for 3 h. The solvent was then removed *in vacuo* and the residue was extracted with boiling chloroform (5 × 10 ml). The chloroform was removed and the residue was extracted with boiling ethyl acetate (4 × 10 ml) giving a residue which was dissolved in water and passed through Amberlite IRA 400 (20 ml), regenerated with *p*-toluenesulfonic acid. Removal of the water and recrystallization from methanol-ether afforded 161 mg (23 %) of 1,3-dimethyl-1,2,3-triazolium tosylate (IIIa) as colourless crystals, m.p. 125 – 127°C. IR- and NMR-spectra were identical with

* It has been found previously that 1,3-disubstituted 1,2,3-triazolium salts do not react with bromine.[21]

Table 3. Spectroscopic data of 1,3-disubstituted-4-(1,2,3-triazolio)sulfides, 1-substituted alkylthio-1,2,3-triazoles, 1-substituted benzoylthio-1,2,3-triazoles, and 1-substituted 4- and 5-mercapto-1,2,3-triazoles.

Compound	IR[a] C—H-4 cm^{-1}	IR[a] C—H-5 cm^{-1}	NMR[b] H-4 ppm	NMR[b] H-5 ppm	NMR[b] NCH_3 ppm	NMR[b] J^{13}_{C-H} Hz	NMR[b] NCH_2 ppm	NMR[b] SCH_3 ppm	NMR[b] J^{13}_{C-H}[c] Hz	NMR[b] SCH_2 ppm
[1,3-Dimethyl-4-(triazolio)] sulfide (Va)		3122		7.58	4.08 4.00	144 143				
[1-Methyl-3-benzyl-4-(triazolio)]sulfide (VIb)		3076		7.57	3.99	145	5.65			
[1-Benzyl-3-methyl-4-(triazolio)]sulfide (Vb)		3062		7.72	3.95	143	5.48			
1-Methyl-4-methylthio-triazole (VIIIa)		3135(m)		7.50	4.10	143		2.54	142	
1-Methyl-4-benzylthio-triazole (VIIIc)		3122(s)		7.30	3.96	143				4.08
1-Benzyl-4-methylthio-triazole (VIIIb)		3135(m)		7.48			5.55	2.52		
1-Benzyl-4-benzylthio-triazole (Xb)		3126(m)					5.46			4.09
1-Methyl-5-methylthio-triazole (VIIa)	3125(m)		7.63		4.05	143		2.46	142	
1-Methyl-5-benzylthio-triazole (VIIb)	3130(w)		7.65		3.62	143				3.90
1-Benzyl-5-methylthio-triazole (VIIc)	3123(w)		7.66				5.59	2.24	143	
1-Benzyl-5-benzylthio-triazole (IXc)	3135(w)		7.51				5.35			3.64
1-Phenyl-5-benzylthio-triazole (VII:R′ = C_6H_5, R = $CH_2C_6H_5$)			7.69							3.88
1-Methyl-4-benzoylthio-triazole (XIa)		3122(s)		8.06	4.22	145				
1-Benzyl-4-benzoylthio-triazole (XIb)		3130(s)		7.95			5.68			
1-Methyl-5-benzoylthio-triazole (XIVa)	3120(m)		7.89		4.05	142				
1-Methyl-4-mercapto-triazole (XIIa)		3132(s)		7.97	4.14	143				
1-Benzyl-4-mercapto-triazole (XIIb)		3132(m)		7.85			5.50			
1-Methyl-5-mercapto-triazole (XVa)	3124(m)		7.75		4.10	145				

[a] IR-spectra were obtained in potassium bromide discs.
[b] NMR-spectra were obtained in deuteriochloroform with TMS as an internal reference.
[c] $J_{^{13}C-H}$ coupling constants for S-CH_3 groups are discussed in the preceding paper.[7]

those of the material described previously.[21] The ethyl acetate extract was filtered through activated carbon. Removal of the ethyl acetate afforded 180 mg (55 %) of [1,3-dimethyl-4-(1,2,3-triazolio)]sulfide (Va) as cream-coloured crystals, m.p. 162 – 167°C. Recrystallization from ethyl acetate raised the melting point to 172 – 173°C. (Found: C 37.11; H 5.41; N 32.63; S 24.66. Calc. for $C_4H_7N_3S$: C 37.19; H 5.46; N 32.53; S 24.82.) NMR-data are given in Table 3. The compound, like other 4-(1,2,3-triazolio)sulfides, did not absorb from 1600 to 1800 cm^{-1} in infrared.

[1-Benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb). Similarly, 1-benzyl-3-methyl-4-bromo-1,2,3-triazolium tosylate (Ib)[4] (1.30 g), sodium sulfide (0.40 g), and dimethylformamide (3.20 ml) after heating with stirring to 100°C for 3 h, removal of the solvent, extraction with chloroform, and removal of the chloroform gave a residue. This was extracted with ethyl acetate leaving a residue, which was dissolved in water and passed through Amberlite IRA 400 (20 ml), regenerated with *p*-toluene sulfonic acid. Removal of the water and recrystallization from methanol-ether afforded 157 mg (15 %) of 1-methyl-3-benzyl-1,2,3-triazolium tosylate (IIIb) as colourless crystals, m.p. 147 – 149°C. IR- and NMR-spectra were identical with those of the material described previously.[4] The ethyl acetate extract was filtered through activated carbon. Removal of the solvent afforded 379 mg of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) as cream-coloured crystals, m.p. 102 – 112°C. Recrystallization from ethyl acetate-ether gave 286 mg (45 %), m.p. 124 – 125°C. Further recrystallization raised the melting point to 129°C. (Found: C 58.32; H 5.56; N 20.30; S 15.45. Calc. for $C_{10}H_{11}N_3S$: C 58.50; H 5.40; N 20.47; S 15.62.) NMR-data are given in Table 3.

The mother liquor from the recrystallization of (Vb) contained a yellow oil which was chromatographed on silica gel (30 g) using ethyl acetate as eluent. The first two fractions did not contain aromatic compounds as shown by NMR. The next fraction contained 42 mg (7 %) of (Vb), m.p. 124 – 126°C. Recrystallization from ethyl acetate raised the melting point to 129°C. IR- and NMR-spectra proved the identity. Thus the total yield of (Vb) is 52 %. The column was then eluted with ethyl acetate – methanol (1:1) yielding 21 mg (3 %) of (VIb), m.p. 130 – 134°C. Recrystallization from ethyl acetate raised the melting point to 137 – 139°C. IR- and NMR-spectra were identical with those of the material described below.

In order to demonstrate that the [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) is stable under the reaction conditions, (Vb) (57 mg), sodium sulfide (36 mg), and dimethylformamide (0.30 ml) were heated with stirring to 100°C for 3 h. The dimethylformamide was removed *in vacuo* and the residue was extracted with chloroform. Removal of the chloroform furnished 57 mg (100 %) of unchanged starting material (Vb), m.p. 127 – 129°C. The identity and purity were proved by IR- and NMR-spectra.

[1-Methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (VIb). Similarly, 1-methyl-3-benzyl-4-bromo-1,2,3-triazolium tosylate (IVb)[4] (2.38 g), sodium sulfide (0.73 g), and dimethylformamide (5.90 ml), after heating with stirring to 100°C for 3 h and working up as described above, afforded 351 mg (18 %) of 1-methyl-3-benzyl-triazolium tosylate (IIIb), identical with the material described previously.[4] The ethyl acetate extract was chromatographed on silica gel (50 g) using ether as eluent. This gave three fractions which were not identified further. The column was then eluted with ethyl acetate. First two minor fractions left the column. Then 138 mg (12 %) of [1-benzyl-3-methyl-4-(1,2,3-triazolio)]-sulfide (Vb) was collected as colourless crystals, m.p. 124 – 126°C. IR- and NMR-spectra proved the identity with the material described above. The column was then eluted with ethyl acetate – methanol (1:1). This gave 350 mg (30 %) of [1-methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (VIb) as colourless crystals, m.p. 118 – 123°C. Recrystallization from ethyl acetate raised the melting point to 137 – 139°C. (Found: C 58.34; H 5.48; N 20.32; S 15.58.) NMR-data are given in Table 3.

[1-Methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd). 1-Methyl-3-phenyl-4-chloro-1,2,3-triazolium tosylate (Id) (482 mg), sodium sulfide (165 mg), and dimethylformamide (1.30 ml) were heated with stirring and worked up as above. The ethyl acetate extract was filtered through activated carbon, the ethyl acetate was removed, and the residue was recrystallized from chloroform – ether giving 234 mg (93 %) of [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd), m.p. 100 – 102°C. Further recrystallization raised the melting point to 112°C. The compound was identical with that described previously.[7]

Dealkylation of 4-(1,2,3-triazolio)sulfides

[1,3-Dimethyl-4-(1,2,3-triazolio)]sulfide (Va) (49 mg) and benzene (0.50 ml) were heated to 180°C in a sealed tube. Removal of the benzene gave 49 mg of a brown oil. An NMR-spectrum indicated the presence of 1-methyl-5-methylthio-1,2,3-triazole (VIIa) and 1-methyl-4-methylthio-1,2,3-triazole (VIIIa) in the ratio 1.6:1, corresponding to 62 % and 38 % yield, respectively. The methylthio-triazoles were separated by preparative TLC eluting four times with ether – hexane (1:1). The compounds were identical with those described below.

[1-Benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) (528 mg) and benzene (5.30 ml) were heated to 180°C for 3 h. Removal of the benzene gave a brown oil which was chromatographed on silica gel (20 g) using ether – hexane (1:1) as eluent. The first fraction contained a minute amount of an unidentified compound. The next fraction contained 18 mg (2 %) of 1-benzyl-4-benzylthio-1,2,3-triazole (Xb) as yellow crystals, m.p. 70 – 71°C. Filtering through activated carbon and recrystallization from ether-hexane gave colourless crystals, m.p. 71°C. (Found: C 68.39; H 5.28. Calc. for $C_{16}H_{15}N_3S$: C 68.32; H 5.37.) Spectroscopic data are given in Table 3. The next fraction contained 431 mg (82 %) of 1-methyl-5-benzylthio-1,2,3-triazole (VIIb). The product was purified as described for (Xb) and gave a colourless oil which could not be induced to crystallize. (Found: C 58.51; H 5.28; N 20.31; S 15.71. Calc. for $C_{10}H_{11}N_3S$: C 58.50; H 5.40; N 20.47; S 15.62.) The next fraction contained 44 mg (13 %) of 1-methyl-5-methylthio-1,2,3-triazole (VIIa). Purification as above gave a colourless oil. (Found: C 37.29; H 5.57; N 32.63. Calc. for $C_4H_7N_3S$: C 37.19; H 5.46; N 32.53.)

[1-Methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (VIb) (317 mg) and benzene (3.20 ml) similarly gave a crude product which was chromatographed on silica gel (30 g) using ether – hexane (1:1) as eluent. The first fraction contained 79 mg (18 %) of 1-benzyl-5-benzylthio-1,2,3-triazole (IXc) as brownish crystals, m.p. 76 – 80°C. Purification as above gave colourless crystals, m.p. 82°C. (Found: C 68.25; H 5.25; N 14.78; S 11.42. Calc. for $C_{16}H_{15}N_3S$: C 68.32; H 5.37; N 14.94; S 11.39.) The next fraction contained 33 mg (10 %) of 1-benzyl-5-methylthio-1,2,3-triazole (VIIc) as a colourless oil. Purification as above gave the pure compound. (Found: C 58.59; H 5.38; N. 20.60; S 15.65. Calc. for $C_{10}H_{11}N_3S$: C 58.50; H 5.40; N 20.47; S 15.62.) The next fraction contained 136 mg (43 %) of 1-methyl-4-benzylthio-1,2,3-triazole (VIIIc) as colourless crystals, m.p. 40 – 41°C. Purification as above raised the melting point to 57°C. (Found: C 58.54; H 5.39; N 20.60; S 15.43.) The column was then eluted with ether. This gave 41 mg (20 %) of 1-methyl-4-methylthio-1,2,3-triazole (VIIIa) as a colourless oil. Purification as above gave the pure material. (Found: C 37.34; H 5.53; N 32.65. Calc. for $C_4H_7N_3S$: C 37.19; H 5.46; N 32.53.)

[1-Methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide. A. (Vd) (17 mg) and benzene (0.40 ml) were heated to 180°C for 3 h. Removal of the benzene gave a brown oil which, as shown by NMR, consisted of a mixture of the starting material (Vd) and 1-phenyl-5-methylthio-1,2,3-triazole (VIId) in the ratio 2.9:1.

B. (Vd) (15 mg) and benzene (0.34 ml) were heated to 190°C for 16 h. Removal of the benzene gave 15 mg (100 %) of 1-phenyl-5-methylthio-1,2,3-triazole (VIId), identical with the material described previously.[9]

[1-Benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) and [1-methyl-3-phenyl-4-(1,2,3-triazolio)]sulfide (Vd), (103 mg) and (95 mg), respectively, were heated with benzene (2.00 ml) to 180°C for 3 h. Removal of the benzene gave a brown oil which was chromatographed on silica gel (20 g) (ether – hexane 1:1). The first fraction contained 36 mg (27 %) of 1-phenyl-5-benzylthio-1,2,3-triazole (VII; $R' = C_6H_5$, $R = CH_2C_6H_5$) as a brown oil. Purification in the usual manner gave a colourless oil. (Found: C 67.37; H 5.03. Calc. for $C_{15}H_{13}N_3S$: C 67.39; H 4.91.) The compound was identified through its NMR-spectrum (Table 3) which, in addition to two phenyl groups, showed a CH-signal and an SCH_2-signal. The next fraction contained a mixture which was separated by preparative TLC eluting twice with benzene – ether (4:1). The first fraction contained 44 mg (46 %) of 1-phenyl-5-methylthio-1,2,3-triazole (VIId), identical with the material described above. The second fraction contained 46 mg (44 %) of 1-methyl-5-benzylthio-1,2,3-triazole (VIIb), identical with the material described above. The third fraction to leave the column contained 14 mg (21 %) of 1-methyl-5-methylthio-1,2,3-triazole (VIIa), identical with the compound described above.

1-Methyl-4-benzylthio-1,2,3-triazole (VIIIc) (25 mg) and benzene (0.25 ml) were heated to 180°C for 3 h. Removal of the benzene gave 23 mg (94 %) of unchanged starting material.

Dealkylation with sodium methoxide

[1-Benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) (372 mg) and 1 N sodium methoxide (5.4 ml) were heated to 180°C for 6 h in a sealed tube. Glacial acetic acid (0.86 ml) was then added and the mixture was worked up as described below for the preparation of 1-methyl-5-mercapto-1,2,3-triazole (XVa). This gave 131 mg of crude XVa which was chromatographed on silica gel (20 g) using ethyl acetate as eluent. The first fraction contained 50 mg (24 %) of XVa, m.p. 92–97°C. Recrystallization raised the melting point to 102°C. The compound was identical with the material prepared below. The combined residues, dissolved in water, were acidified with conc. hydrochloric acid (0.86 ml) as described below giving 99 mg (48 %) of impure 5-methylamino-1,2,3-thiadiazole (XVIa). Purification was difficult in this case. The product was therefore converted to its hydrochloride (see below) which was easily recrystallized from methanol–ether. The material was identical with the hydrochloride of (XVIa) described below.

Dealkylation with sodium methoxide followed by realkylation with methyl iodide

[1-Benzyl-3-methyl-4-(1,2,3-triatzolio)]sulfide (Vb) (111 mg) and 1 N sodium methoxide (1.70 ml) were heated to 180°C for 6 h in a sealed tube. The mixture was cooled to room temperature, methyl iodide (0.24 ml) was added, and the mixture was kept at room temperature for 3 h. The mixture was then evaporated to dryness and water (10 ml) was added. The solution was extracted with methylene chloride (3 × 10 ml), the combined extracts were dried (magnesium sulfate), the solvent was removed, and the residue was dissolved in ethyl acetate and filtered through activated carbon. Removal of the ethyl acetate afforded 63 mg (90 %) of 1-methyl-5-methylthio-1,2,3-triazole (VIIa), identical with the material described above as shown by its spectra.

[1-Methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (Vc). Similarly, Vc (141 mg), 1 N sodium methoxide (2.16 ml), and methyl iodide (0.31 ml) gave a methylene chloride extract. This contained an oil which was chromatographed on silica gel (10 g) using ether–hexane (1:1) as eluent. The first fraction contained 89 mg (63 %) of 1-benzyl-5-methylthio-1,2,3-triazole (VIIc), identical with the material described above as shown by the spectra.

Preparation of benzoylthio-1,2,3-triazoles

[1-Benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb) (0.97 g), pyridine (0.78 ml), and benzoyl chloride (7.20 ml) were heated to 100°C for 90 min. Hexane (72 ml) was then added and the mixture was kept overnight at −30°C. The precipitate was filtered off, washed with hexane (3 × 5 ml), and extracted with five 10 ml portions of boiling benzene–ether (4:1). The extracts were successively poured onto a column of silica gel (60 g) which was subsequently eluted with benzene–ether (4:1). The first fraction contained a minor amount of benzoyl chloride. The next fraction contained 447 mg (32 %) of 1-benzyl-4-benzoylthio-1,2,3-triazole (XIb) as colourless crystals, m.p. 142–147°C. Recrystallization from ethyl acetate-ether raised the melting point to 153–154°C. (Found: C 65.25; H 4.47; N 14.38; S 10.82. Calc. for $C_{16}H_{13}N_3OS$: C 65.06; H 4.44; N 14.23; S 10.86.) The second fraction contained 511 mg (49 %) of 1-methyl-5-benzoylthio-1,2,3-triazole (XIVa) as colourless crystals, m.p. 138–147°C. Recrystallization from ethyl acetate–ether raised the melting point to 152–153°C. (Found: C 54.68; H 4.24; N 19.35; S 14.72. Calc. for $C_{10}H_9N_3OS$: C 54.78; H 4.14; N 19.17; S 14.62.)

[1-Methyl-3-benzyl-4-(1,2,3-triazolio)]sulfide (VIc) (171 mg), pyridine (0.14 ml), and benzoylchloride (1.30 ml) were heated to 100°C for 90 min and the mixture was worked up as described above. The precipitate was extracted with boiling ether (5 × 10 ml). Removal of the ether and recrystallization from ethyl acetate–ether gave 82 mg (45 %)

of 1-methyl-4-benzoylthio-1,2,3-triazole (XIa) as colourless crystals, m.p. 114°C. One further recrystallization raised the melting point to 119°C. (Found: C 54.96; H 4.18; N 19.25; S 14.53. Calc. for $C_{10}H_9N_3OS$: C 54.78; H 4.14; N 19.17; S 14.62.) A higher yield was obtained by chromatography of the ether-extract on silica gel (18 g) using ether as eluent. The first fraction contained benzoyl chloride. The next fraction contained 114 mg (63 %) of (XIa), m.p. 110–112°C. One recrystallization raised the melting point to 119°C.

[*1,3-Dimethyl-4-(1,2,3-triazolio)*]*sulfide (Va)* (93 mg), pyridine (0.06 ml), and benzoyl chloride (0.70 ml) were heated to 180°C for 115 min, and the mixture was worked up as above. The crude precipitate was purified by preparative TLC eluting twice with ethyl acetate–hexane (1:3). The fast running fraction contained 28 mg (18 %) of 1-methyl-5-benzoylthio-1,2,3-triazole (XIVa) as colourless crystals, m.p. 149–150°C. Recrystallization from ethyl acetate–ether raised the melting point to 152–153°C. M.p., IR-, and NMR-spectra were identical with those of the material described above. The next fraction contained 89 mg (57 %) of 1-methyl-4-benzoylthio-1,2,3-triazole (XIa) as colourless crystals, m.p. 114°C. Recrystallization from ethyl acetate–ether raised the melting point to 119°C. M.p., IR-, and NMR-spectra proved the identity with the material described above.

Preparation of mercapto-1,2,3-triazoles

1-Methyl-5-mercapto-1,2,3-triazole (XVa). 1-Methyl-5-benzoylthio-1,2,3-triazole (XIVa) (442 mg) and 1 N sodium hydroxide (4.10 ml) were heated to reflux for 3 h. The solution was acidified with glacial acetic acid (0.80 ml) and the water was removed *in vacuo*. The residue was extracted with boiling ethyl acetate (5 × 10 ml). Removal of the ethyl acetate gave colourless crystals which were extracted with boiling ether (10 × 20 ml). The volume of the combined extracts was reduced to 20 ml. Hexane (40 ml) was added and the mixture was cooled to −30°C. This afforded 68 mg (29 %) of 1-methyl-5-mercapto-1,2,3-triazole (XVa) as a colourless oil which crystallized on standing, m.p. 102°C. Further recrystallization did not raise the melting point. (Found: C 31.47; H 4.18; N 36.43; S 28.01. Calc. for $C_3H_5N_3S$: C 31.28; H 4.37; N 36.48; S 27.83.) Equiv. weight found by potentiometric titration with 0.1 N aqueous sodium hydroxide: 116.3 (calc. 115.2). pK_a in aqueous solution 8.3. The combined residues from the extractions with ethyl acetate and with ether were dissolved in water (20 ml) and conc. hydrochloric acid (0.80 ml) was added. The mixture was evaporated to dryness and extracted with ethyl acetate (5 × 10 ml). Removal of the ethyl acetate and recrystallization from ethyl acetate–hexane gave 166 mg (71 %) of 5-methylamino-1,2,3-thiadiazole (XVIa) as colourless crystals, m.p. 78–97°C. One more recrystallization yielded 121 mg (52 %), m.p. 108–110°C. Further recrystallization raised the melting point to 119–121°C. (Found: C 31.42; H 4.45; N 36.39; S 27.69.) NMR ($CDCl_3$, TMS): CH δ 7.70; NH δ 4.63; NCH_3 δ 4.10, J^{13}_{C-H} 143. The IR-spectrum was different from that of 1-methyl-5-mercapto-1,2,3-triazole (XVa). The hydrochloride of (XVIa) was prepared by dissolving 1-methyl-5-mercapto-1,2,3-triazole (XVa) or 5-methylamino-1,2,3-thiadiazole (XVIa) in methanol. Ethereal hydrogen chloride was added in excess and the solution was filtered giving the hydrochloride of (XVIa) in quantitative yield as colourless crystals, m.p. 143–145°C. Further recrystallization from methanol–ether raised the melting point to 149–151°C. (Found: C 23.96; H 3.88; N 27.89; S 21.42; Cl 23.25. Calc. for $C_3H_6N_3SCl$: C 23.76; H 3.99; N 27.73; S 21.16; Cl 23.39.)

1-Methyl-4-mercapto-1,2,3-triazole (XIIa). 1-Methyl-4-benzoylthio-1,2,3-triazole (XIa) (174 mg) and 1 N sodium hydroxide (1.55 ml) were heated to reflux for 90 min. Methylene chloride (10 ml) was then added and the mixture was acidified with hydrochloric acid to pH = 2.5. The organic layer was separated and the water phase was extracted twice with methylene chloride (10 ml). The combined extracts were dried (magnesium sulfate), the methylene chloride was removed, and the residue was heated to boiling with ether (10 ml). The mixture was cooled to −30°C and the precipitate was filtered off. This extraction with ether was repeated once more giving 83 mg (91 %) of 1-methyl-4-mercapto-1,2,3-triazole (XIIa) as colourless crystals, m.p. 117–119°C. Recrystallization from ethyl acetate–ether raised the melting point to 124–125°C. (Found: C 31.48; H 4.51; N 36.32; S 27.93. Calc. for $C_3H_5N_3S$: C 31.28; H 4.37; N 36.48; S 27.83.)

1-Benzyl-4-mercapto-1,2,3-triazole (XIIb). Similarly, 1-benzyl-4-benzoylthio-1,2,3-triazole (XIb) (217 mg) and 1 N sodium hydroxide (1.70 ml) were heated to reflux for 90 min. Methylene chloride was added and the mixture was acidified to pH = 2.5. Extraction with methylene chloride and removal of the methylene chloride gave a residue which was purified by TLC (one plate) eluting twice with ether. The fraction with high R_F-value contained benzoic acid. The fraction with low R_F-value contained 131 mg (93 %) of 1-benzyl-4-mercapto-1,2,3-triazole (XIIb) as a colourless oil which crystallized on standing, m.p. 71°C. Recrystallization from ethyl acetate – ether raised the melting point to 72 – 73°C. (Found: C 56.55; H 4.74; N 22.18; S 16.67. Calc. for $C_9H_9N_3S$: C 56.53; H 4.75; N 21.98; S 16.78.)

Attempts to rearrange mercapto-1,2,3-triazoles

1-Methyl-5-mercapto-1,2,3-triazole (XVa). A. XVa (16.0 mg) and glacial acetic acid (1.00 ml) were heated to reflux for 1 h. The acetic acid was then removed *in vacuo* leaving 13.3 mg (83 %) of unchanged starting material as a yellow oil. Crystallization from ether-hexane afforded 12.9 mg, m.p. 97 – 100°C. IR- and NMR-spectra proved the identity.

B. XVa (51 mg) was dissolved with heating in 1 N hydrochloric acid (5.00 ml). Evaporation to dryness *in vacuo* gave 66 mg (97 %) of the hydrochloride of 5-methylamino-1,2,3-thiadiazole, m.p. 144 – 145°C, identical with the material described above.

1-Benzyl-4-mercapto-1,2,3-triazole (XIIb) (49 mg) and 1 N hydrochloric acid (2.00 ml) were heated to reflux for 1 h. The solution was evaporated to dryness *in vacuo* leaving 48 mg (97 %) of unchanged starting material as an oil which crystallized on standing.

Methylation of mercapto-triazoles

1-Benzyl-4-mercapto-1,2,3-triazole (XIIb) (141 mg) was dissolved in 1 N sodium methoxide (1.50 ml); methyl iodide (1.40 ml) was added, and the mixture was kept at room temperature for 3 h. Evaporation to dryness *in vacuo*, addition of water (10 ml), extraction with methylene chloride (3 × 10 ml), drying of the methylene chloride extract (magnesium sulfate), and removal of the methylene chloride gave 121 mg (80 %) of 1-benzyl-4-methylthio-1,2,3-triazole (VIIIb), m.p. 57 – 60°C. The product was dissolved in ethyl acetate and filtered through activated carbon. The ethyl acetate was removed and the residue was recrystallized from ether-hexane. This gave pure XIIb as colourless crystals, m.p. 60 – 62°C. (Found: C 58.31; H 5.42; N 20.56; S 15.47. Calc. for $C_{10}H_{11}N_3S$: C 58.50; H 5.40; N 20.47; S 15.62.)

1-Methyl-5-mercapto-1,2,3-triazole (XVa). Similarly, XVa (53 mg), 1 N sodium methoxide (0.92 ml), and methyl iodide (0.86 ml) gave a methylene chloride extract which contained 46 mg (78 %) of 1-methyl-5-methylthio-1,2,3-triazole (VIIa). IR- and NMR-spectra proved the identity with the material described above.

Preparation and reactions of 1-benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide (XVIIb)

1-Benzyl-3-menthyl-4-(1,2,3-triazolio)sulfide (Vb) (273 mg) was dissolved in dry chloroform (5.40 ml) and bromine (0.085 ml) was added with stirring at room temperature. The stirring was continued for 10 min. The precipitate was then filtered off and washed with chloroform (3 × 1 ml). The product was dried at atmospheric pressure over phosphorus pentoxide. This gave 484 mg (100 %) of 1-benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide as orange, hygroscopic crystals, m.p. 137 – 138°C. The compound could not be purified by recrystallization and a correct analysis could therefore not be obtained. The NMR-spectrum (DMSO-d_6, TMS) showed a single proton at δ 9.35, a phenyl group at δ 7.50, a CH_2-signal at δ 5.95, and a CH_3 signal at δ 4.32.

1-Benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide (XVIIb) and [1-benzyl-3-methyl-4-(1,2,3-triazolio)]sulfide (Vb). A mixture of XVIIb (94 mg), Vb (54 mg), and chloroform (5.00 ml) was stirred at room temperature for 15 min. The homogeneous solution formed was evaporated to dryness *in vacuo*. The residue thus obtained was reprecipitated from methanol-ether. This gave 150 mg (100 %) of di[1-benzyl-3-methyl-4-(1,2,3-triazolium)]disulfide dibromide (XIXb) as a yellow oil. The compound is very

hygroscopic and a correct analysis could not be obtained. (Found: C 40.24; H 4.03; N 13.49; S 10.32; Br 28.27. Calc. for $C_{20}H_{22}N_6S_2Br_2.H_2O$: C 42.11; H 3.89; N 14.75; S 11.25; Br 28.02.) The NMR-spectrum (DMSO-d_6, TMS) showed a singlet at δ 10.04 due to the two heteroaromatic protons. The two phenyl groups absorbed at δ 7.8 – 7.3 (complex multiplet). The two CH_2-groups and the two CH_3-groups gave rise to singlets at δ 6.05 and 4.36, respectively.

1-Benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide (XVIIb) and acetone. XVIIb (140 mg) was dissolved in acetone (15 ml) and the colourless solution was immediately evaporated to dryness *in vacuo* giving 131 mg (100 %) of 1-benzyl-3-methyl-4-acetylmethylthio-1,2,3-triazolium bromide (XVIIIb, R″ = CH_2COCH_3), as a colourless oil which was reprecipitated from methanol – ether furnishing the pure compound. The product is hygroscopic and a correct analysis could not be obtained. The NMR-spectrum (DMSO-d_6, TMS) showed a single proton at δ 9.22, a phenyl group signal at δ 7.50, a CH_2-signal at δ 5.93, and a CH_3-signal at δ 4.28. The CH_2CO protons absorbed at δ 4.43 and the CH_3CO protons resonated at δ 2.23.

1-Benzyl-3-methyl-4-bromothio-1,2,3-triazolium bromide (XVIIb) and cyclohexene. A mixture of XVIIb (100 mg), cyclohexene (33 μl), and chloroform (5.00 ml) was stirred at room temperature. The sulfenyl bromide XVIIb went into solution and the solution turned colourless. After 15 min the solvent was removed *in vacuo* giving 1-benzyl-3-methyl-4-(2-bromocyclohexylthio)-1,2,3-triazolium bromide (XVIIIb, R″ = 2-bromocyclohexyl) as a colourless oil in quantitative yield. The compound is unstable and could not be purified by reprecipitation. The NMR-spectrum (DMSO-d_6, TMS) showed a single proton at δ 9.67, a phenyl group signal at δ 7.50 (broad singlet), a CH_2-signal at δ 6.08, and a CH_3-signal at δ 4.34. The two protons adjacent to the sulfur- and to the bromine atom in the cyclohexane ring gave rise to a multiplet at δ 4.62 – 4.17. The remaining 8 protons of the cyclohexane ring gave rise to a broad absorption from δ 2.4 to 1.1.

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REFERENCES

1. Begtrup, M. *Tetrahedron Letters* **1971** 1577.
2. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **20** (1966) 1555.
3. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **23** (1969) 1091.
4. Begtrup, M. *Acta Chem. Scand.* **25** (1971) 249.
5. Begtrup, M. *Acta Chem. Scand.* **25** (1971) 803.
6. Begtrup, M. *Unpublished results.*
7. Begtrup, M. *Acta Chem. Scand.* **25** (1971) 3500.
8. Begtrup, M. *Acta Chem. Scand.* **25** (1971) 795.
9. Pedersen, C. and Kindt-Larsen, T. *Acta Chem. Scand.* **16** (1962) 1800.
10. Regitz, M. and Liedhegener, A. *Ann.* **710** (1967) 118.
11. Regitz, M. and Scherer, H. *Chem. Ber.* **102** (1969) 417.
12. Albert, A. and Tratt, K. *Angew. Chem.* **78** (1966) 596.
13. Brown, D. J. and Paddon-Row, M. N. *J. Chem. Soc.* **C 1967** 1856.
14. Albert, A. *J. Chem. Soc.* **C 1969** 152.
15. Dimroth, O. *Ann.* **335** (1904) 6.
16. Dimroth, O. *Ann.* **373** (1910) 336.
17. A recent review on the Dimroth-rearrangement is available: Wahren, M. *Z. Chem.* **9** (1969) 241.
18. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **21** (1967) 633.
19. Kharasch, N., Potempa, S. J. and Wehrmeister, H. L. *Chem. Rev.* **39** (1946) 269.
20. Magee, P. S. In Senning, A., Ed., *Sulfur in Organic and Inorganic Chemistry*, Marcel Dekker, New York 1971, Vol. 1, p. 256.
21. Begtrup, M. and Kristensen, P. A. *Acta Chem. Scand.* **23** (1969) 2733.
22. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **19** (1965) 2022.
23. Dimroth, O. *Ann.* **364** (1909) 203.
24. Lieber, E., Chao, T. S. and Ramachandra Rao, C. N. *J. Org. Chem.* **22** (1957) 654.

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