Tetrahedron Letters No.19, pp. 1577-1578, 1971. Pergamon Press. Printed in Great Britain.

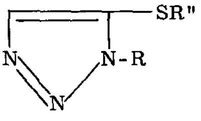
4-(1, 2, 3-TRIAZOLIO)SULFIDES, A NEW MESOIONIC SYSTEM

Mikael Begtrup
Department of Organic Chemistry, Technical University
of Denmark, DK-2800 Lyngby, Denmark

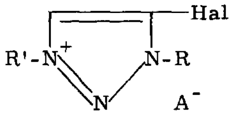
(Received in UK 25 March 1971; accepted for publication 1 April 1971)

The synthesis of 4-(1, 2, 3-triazolio)oxides 3 has been described previously.[1a-f] These compounds were prepared by (i) alkylation of 1-substituted 4- or 5-hydroxy-1, 2, 3-triazoles,[1a-e] (ii) rearrangement of 1-substituted 4- or 5-methoxy-1, 2, 3-triazoles,[1b-c] and (iii) displacement of halogen from 1, 3-disubstituted 4-halo-1, 2, 3-triazolium salts 2.[1f-g] Recently, a direct ring closure of N-methyl-N-arylazoaminoacetates has been reported,[2] additional to these methods. The three first approaches have now been investigated with a view to preparing the 4-(1, 2, 3-triazolio)sulfides 6. It was found that method (i) could not be used since methylation of 1-substituted 4- or 5-mercapto-1, 2, 3-triazoles with methyl iodide gave the S-methyl derivatives 4 or 1 exclusively.[3] Method (ii) was however applicable since 4 or 1, when treated with methyl tosylate, gave 1, 3-disubstituted 4-methylthio-1, 2, 3, -triazolium salts 5 which, on heating with piperidine, dealkylated to 4-(1, 2, 3-triazolio)sulfides 6.[3] Method (iii) turned out to be the most convenient. Thus treatment of 1, 3-disubstituted 4-halo-1, 2, 3-triazolium salts 2, with sodium sulfide in dimethyl formamide, gave 4-(1, 2, 3-triazolio)sulfides 6 in good yields (Table 1).

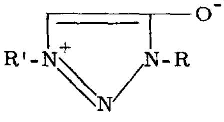
Generally, 4-(1, 2, 3-triazolio)oxides 3 are stable even by prolonged heating to 200° in an inert solvent. In contrast, 4-(1, 2, 3-triazolio)sulfides 6 rearrange when heated in benzene solution to 180° for 3 h. Thus [1-benzyl-3-methyl-4-(1, 2, 3-triazolio)] sulfide 6 ($R=CH_3$, $R'=CH_2C_6H_5$) produces a chromatographically separable mixture of 1-methyl-5-benzylthio-1, 2, 3-triazole 1 ($R=CH_3$, $R''=CH_2C_6H_5$) (82 %, oil), 1-benzyl-4-benzylthio-1, 2, 3-triazole 4 ($R'=R''=CH_2C_6H_5$) (2 %, m. p. 71°), and 1-methyl-5-methylthio-1, 2, 3-triazole 1 ($R=R''=CH_3$) (13 %, oil). The formation of the last two compounds suggests an intermolecular alkyl group transfer reaction. The 4-(1, 2, 3-triazolio)sulfides 6 are readily methylated to give 1, 3-disubstituted 4-methylthio-1, 2, 3-triazolium salts 5 ($R''=CH_3$).[3]



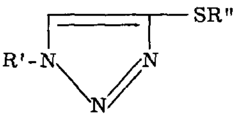
1



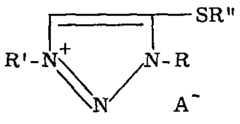
2



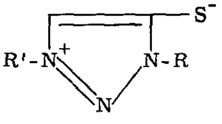
3



4



5



6

Similarly, 6 are readily acylated. Thus [1-benzyl-3-methyl-4-(1, 2, 3-triazolio)] sulfide 6 ($R=CH_3$, $R'=CH_2C_6H_5$), when heated with benzoylchloride and pyridine,produces a chromatographically separable mixture of 1-methyl-5-benzoylthio-1, 2, 3-triazole 1 ($R=CH_3$, $R''=COC_6H_5$)(49 %, m.p. 152-153°) and 1-benzyl-4-benzoylthio-1, 2, 3-triazole 4 ($R'=CH_2C_6H_5$, $R''=COC_6H_5$) (32 %, m.p. 153-154°). Probably, 6 and benzoyl chloride first give the 4-benzoylthio compound 5 ($R''=COC_6H_5$) which, in its turn, suffers dealkylation under the reaction conditions. A similar course of reactions has been noted in the 4-(1, 2, 3-triazolio)oxide series.[1d-e]

Table 1: Preparation of 4-(1, 2, 3-triazolio)sulfides 6 from 1, 3-disubstituted 4-halo-1, 2, 3-triazolium salts 2

Starting material 2	Product[4] 6	Yield %	m.p.
$R=R'=CH_3$, Hal=Br	$R=R'=CH_3$	55	172-173°
$R=CH_3$, $R'=CH_2C_6H_5$, Hal=Br	$R=CH_3$, $R'=CH_2C_6H_5$	43	129°
$R=CH_2C_6R_5$, $R'=CH_3$, Hal=Br	$R=CH_2C_6H_5$, $R'=CH_3$	30	137-139°
$R=C_6H_5$, $R'=CH_3$, Hal=Cl	$R=C_6H_5$, $R'=CH_3$	93	112°

References

1) a) M. Begtrup and C. Pedersen, Acta Chem. Scand. 19, 2022 (1965). b) ibid. 20, 1555 (1966). c) ibid. 21, 633 (1967). d) ibid. 21, 1234 (1967). e) ibid. 23, 1091 (1969). f) M. Begtrup and P. A. Kristensen, ibid. 23, 2733 (1969). g) M. Begtrup, ibid. In press.

2. K. T. Potts and S. Husain, J. Org. Chem. 35, 3451 (1970).

3. M. Begtrup, Acta Chem. Scand., In press.

4. Combustion analyses of all compounds were within 0. 3 % of theory. All compounds gave consistent NMR-spectra.