Five-membered Heterocyclic Thiones. Part VI (1).
2-Methyl-1,2,3-triazole-4-thiol

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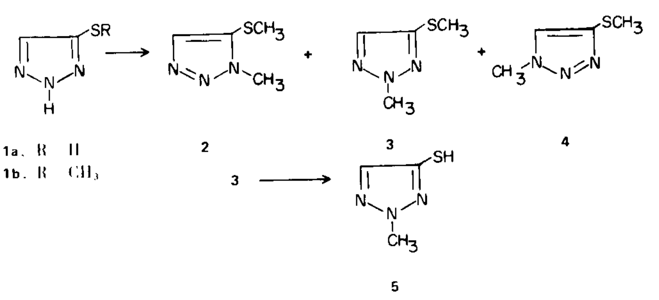
Although the first 1,2,3-triazolethiol (thione) was synthesised in 1909 (3), it is only comparatively recently that synthetic interest has been revived in this area (4-9). The majority of the known triazolethiols have been prepared by the thiolation of a chloro-1,2,3-triazole (3-5), or by a Dimroth type of rearrangement (10) of a 5-amino-1,2,3-thiadiazole (3-8). The latter reaction has considerable versatility, and both *N*-unsubstituted 1,2,3-triazole-4-thiols (including the parent compound) and 1-substituted-1,2,3-triazole-5-thiols have been obtained thereby. The rearrangement cannot, however, be applied to the preparation of 1- or 2-substituted-1,2,3-triazole-4-thiols. In this connection, Begtrup (9) has recently devised an ingenious synthesis of 1-substituted-1,2,3-triazole-4-thiols (as well as 1-substituted-1,2,3-triazole-5-thiols) from mesoionic 1,3-disubstituted-4-(1,2,3-triazolio) sulfides. This paper describes the synthesis of the first known 2-substituted-1,2,3-triazole-4-thiol.

1,2,3-Triazole-4-thiol (**1a**) was converted into the *S*-methyl ether (**1b**), and the latter, on reaction with ethereal diazomethane, gave a mixture of the three possible *N*,*S*-dimethyl compounds **2**, **3**, and **4**. Two of the components of the mixture had nmr spectra identical to those described by Begtrup (10,11) for compounds **2** and **4**. The other isomer **3**, which constituted approximately 50% of the mixture, was easily separated by fractional distillation (12). Reduction of this dimethyl compound with sodium in liquid ammonia gave the malodorous liquid (**5**) which was different from the two known (9) crystalline *N*-methyl-1,2,3-triazole thiols (14). The most remarkable property of this compound was that it showed a strong infrared absorption at 2540 cm^{-1} in the liquid phase [*i.e.* neat (15)] and a medium intensity band at 2545 cm^{-1} in chloroform solution. This is one of the very few [see ref. 18] examples of the existence of the thiol form in a heteroaromatic system containing the undisturbed -NH-C = S grouping. Several 1-aryl-4-acyl-1,2,3-triazoles containing potential mercapto groups have recently (7) been shown to exist as thiols, but in these cases, the thiol form must, at least in part, be stabilized by hydrogen bonding [ν SH (potassium bromide) 2451-2469 cm^{-1}] to the adjacent acyl group. 1,2,3-Triazole-4-thiol is purported (6) to show infrared bands in the 2500-2590 cm^{-1} region, thus indicating the presence of the thiol form. Although we have prepared this compound many times, we have never obtained infrared spectroscopic evidence (absence of absorptions in the 2500-2600 cm^{-1} region) in support of the above contention. The ultraviolet spectrum (see Table) may, however, indicate the presence of a small amount of the thiol form in methanol solution. 1-Phenyl-1,2,3-triazole-4-thiol is stated (6) to exist in the thiol form (ir evidence). In addition, 1-methyl-1,2,3-triazole-4-thiol and 2-phenyl-1,2,3-triazole-4-thiol have very low intensity absorptions at 2415 and 2418 cm^{-1}, respectively (19), indicative perhaps of a small amount of the thiol form.



Table

Ultraviolet Spectra of some 1,2,3-Triazole Thiols and Related Compounds (a)

Compound	λ max (mμ)	ε max (log ε)
1a	228 290 sh.	3.67 2.71
1a Potassium salt	251	3.52
1b	249	3.44
3	233 256	3.55 3.67
5	238 (b)	3.71
5 Sodium salt (c)	279	3.58

(a) Measured with a Beckman DK-2 uv spectrophotometer as methanol solutions. (b) This band tails to about 300 mμ and has an intensity of 3.55 (log ε) at 256 mμ. (c) This spectrum is that of the thiol in methanol which was 0.05*N* in sodium hydroxide.

EXPERIMENTAL

The melting points were determined in a Gallenkamp melting point apparatus and are not corrected. The infrared spectra were recorded with a Unicam SP-200G ir spectrophotometer. The nmr spectra were measured as chloroform solutions with a Varian A-60A spectrometer. The chemical shifts are expressed as ppm (δ) from internal tetramethylsilane.

4-Methylthio-1,2,3-triazole (**1b**).

To an ethanolic solution of 1,2,3-triazole-4-thiol (4.18 g., 41.3 mmoles (6)) was added an equimolar amount of ethanolic 1.8 *N* potassium hydroxide followed by a small excess (6.4 g., 45 mmoles) of methyl iodide. After ½ hour the solvent was evaporated, the residue was slurried with water, and the product was extracted into dichloromethane. The extract was dried over sodium sulfate and then evaporated *in vacuo* to give a solid (4.09 g., 86%) with m.p. 38-42°. The nmr spectrum had three singlets at δ 2.53 (3H), 7.62 (1H), and 12.88 (1H). After sublimation at 37°/0.001 mm, the triazole had m.p. 46-48°.

Anal. Calcd. for $C_3H_5N_3S$: C, 31.29; H, 4.37; N, 36.49. Found: C, 31.05; H, 4.41; N, 36.52.

Reaction of 4-Methylthio-1,2,3-triazole with Diazomethane.

An ice cold 0.86 *N* ethereal diazomethane solution (225 ml.) was added to a chilled (0°) solution of the *S*-methyl compound (**1b**) (20.88 g., 182 mmoles) in ether. When the evolution of nitrogen had ceased (*ca.* 1 hour) the solvent was removed *in vacuo* and the residue was fractionally distilled. The most volatile material, b.p. 91-94°/23 mm was collected (9.0 g., 38%). The nmr spectrum of this material consisted of three singlets at δ 2.53 (3H), 4.20 (3H), and 7.55 (1H). The still residue (10.65 g.) contained a mixture of the three possible *N,S*-dimethyl-1,2,3-triazoles, two components of which had nmr spectra identical to the known compounds described by Begtrup (9). A small sample of compound **3** was redistilled for analysis.

Anal. Calcd. for $C_4H_7N_3S$: C, 37.19; H, 5.46; N, 32.53. Found: C, 37.15; H, 5.55; N, 32.69.

2-Methyl-1,2,3-triazole-4-thiol (**5**).

This reaction gave acceptable yields only when carried out on a small scale.

Metallic sodium (0.690 g., 30 mmoles) was added in small portions to a stirred solution of the above *N,S*-dimethyl compound (**3**) (1.93 g., 15 mmoles) in liquid ammonia (*ca.* 50 ml.). Ammonium chloride (1.6 g.) was then added, and the ammonia was allowed to evaporate. The residue was dissolved in water to which there had been added 2.5 *N* sodium hydroxide (7.5 ml.) and the solution was extracted with ethyl acetate. The aqueous phase was made strongly acidic (*p*H ~ 1) with concentrated hydrochloric acid and the product was extracted into ethyl acetate. The dried extract was evaporated *in vacuo* and the residue was evaporatively distilled at 95-100°/22 mm to give an oil (0.708 g., 41%) the nmr spectrum of which had singlets at δ 3.50 (1H, W_H = 10 Hz, disappeared on addition of deuterium oxide), 4.18 (3H), and 7.54 (1H). For analysis the oil was distilled, b.p. 78-80°/21 mm.

Anal. Calcd. for $C_3H_5N_3S$: C, 31.29; H, 4.38; N, 36.49. Found: C, 31.58; H, 4.27; N, 36.57.

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(11) We thank Professor Begtrup (Technical University of Denmark) for a preprint of this publication.

(12) 1,2,3-Triazoles which are substituted on the central nitrogen atom are known (13) to be much more volatile than those which bear the same substituent on either of the lateral nitrogen atoms.

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(14) Professor Begtrup has informed us that he too has succeeded in synthesising this compound, as well as the 2-phenyl analogue, *via* a different route.

(15) The SH stretching absorption for thiophene-2 and 3-thiols occurs at 2510-2540 cm^{-1} (16) while isoxazole-5-thiols show a band at 2550 cm^{-1} (17).

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