# Imidazole Thiol-esters from 6-Methylthiopurines, and a 1,2,3-Triazole Thio-imidate from a 6-Methylthio-8-azapurine[†]

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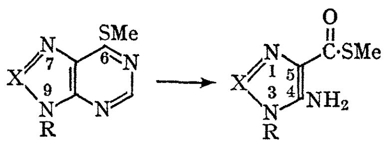
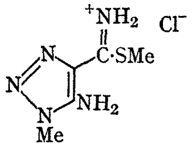
*Summary* The action of acid on 6-methylthiopurines gave the first imidazole thiol-esters, and 9-methyl-6-methylthio-8-azapurine gave the unusual 1,2,3-triazole thioimidate (III); these have potential value as intermediates.

IT was recently shown[1] that 6-methylthio-8-azapurine (Ia) gives, quantitatively, the thiol-ester, 4-amino-5-(methylthio)carbonyl-1,2,3-triazole (IIa) when boiled with 1N-hydrochloric acid. It is now found that 6-methylthiopurine (Ib) similarly gives 4-amino-5-(methylthio)carbonylimidazole (IIb), m.p. 226°, which can be converted by aqueous ammonia into 4-aminoimidazole-5-carboxamide,[2] m.p. 169—170°. Similarly, the purine (Ic) furnishes the thiol-ester (IIc), m.p. 268°. Both thiol-esters showed strong i.r. absorption near 1640 (C–O stretch) and 890 (C–S stretch) cm.$^{-1}$.



(I) (II)

| | X | R |
|---|---|---|
| (a) | N | H |
| (b) | CH | H |
| (c) | CH | Me |
| (d) | N | Me |



(III)

No intermediate was obtained from this purine reaction, but the course of the reaction is indicated by the thioimidate (III) [4-amino-5-*C*-imino-*C*(methylthio)methyl-3-methyl-1,2,3-triazole hydrochloride], now isolated (60% yield) from the reaction (Id) → (IId) when conducted at 25°. This salt had m.p. 207° (from water–acetone). The free base, liberated at pH 7, decomposed on gentle heating to 4-amino-5-cyano-3-methyl-1,2,3-triazole, m.p. 229° (from water) and methanethiol.

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[†] Although contrary to I.U.P.A.C. nomenclature, "8-azapurine" is permitted as a trivial name because of its widespread use in biological work.

[1] A. Albert, *Angew. Chem.*, 1969, **81**, 115.
[2] E. Shaw and D. W. Woolley, *J. Biol. Chem.*, 1949, **181**, 89.

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