# Reaction of Primary Alkyl Azides with Phenyl Isothiocyanate

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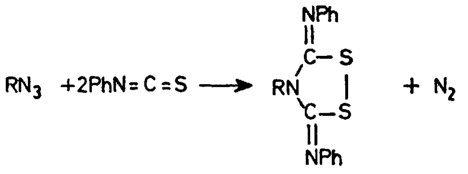
*Summary* The reaction of primary alkyl azides with phenyl isothiocyanate gives 4-alkyl-3,5-bis(phenylimino)-1,2,4-dithiazolidines as the main product.

HYDRAZOIC ACID and sodium azide react with phenyl isothiocyanate to form 5-phenylamino-1,2,3,4-thiatriazole and 1-phenyl-1,2,3,4-tetrazoline-5-thione respectively.[1] Tri-n-butyltin azide and triphenyltin azide give the corresponding 1:1 adducts.[2] Alkyl azides react with equimolar amounts of sulphonyl isothiocyanates to yield the 1,3-dipolar cycloaddition products, 4-alkyl-5-sulphonylimino-1,2,3,4-thiatriazolines.[3]



(1)

**a**; R = Me[CH$_2$]$_3$
**b**; R = Me[CH$_2$]$_4$
**c**; R = Me$_2$CH[CH$_2$]$_3$
**d**; R = EtCH(Me)CH$_2$
**e**; R = Me[CH$_2$]$_5$
**f**; R = PhCH$_2$
**g**; R = C$_{10}$H$_7$CH$_2$

Primary alkyl azides are now shown to react with phenyl isothiocyanate in 1:2 molar ratios giving 4-alkyl-3,5-bis-(phenylimino)-1,2,4-dithiazolidines (**1**) in 29—65% yield. Traces of 4-phenyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**2**) are formed in the preparation of (**1a**—**e**). The yellow, crystalline dithiazolidines are isolated after heating the pure reactants at 80—100 °C in the absence of solvent. The low solubility of (**2**) in light petroleum (b.p. 40—60 °C) enables efficient separation from (**1a**—**e**).

All products are characterised by i.r. [$\nu_{max}$ (KBr) 1610 and 1580 (C=N), and 1300 (C–N) cm$^{-1}$][4] and mass spectral data and by a single crystal *X*-ray analysis of (**1f**; R = PhCH$_2$). A *m/e* 285 ion, common to all mass spectra, represents replacement of the alkyl (**1a**—**g**) or phenyl groups (**2**) attached to the ring nitrogen atom of the molecular ion by a hydrogen atom. Two important fragmentations from this ion, *m/e* 167 and *m/e* 118, can be explained by cleavage of the S(2)–C(3) and N(4)–C(5) bonds of the dithiazolidine ring.

The reaction mechanism may involve stepwise addition of the 2 molecules of PhNCS *via* a 3-membered ring intermediate, $\mathrm{R\overline{N{-}S{-}C}{=}NPh}$. A similar route has been proposed for the formation of 1-phenyl-5-phenylimino-1,2,4-dithiazolidine-3-thione by the reaction of PhN$_3$ with CS$_2$ in the presence of AlCl$_3$. The formation of (**2**) is not yet understood. Under identical conditions transfer of a phenyl group from PhNCS to (**1a**—**e**) does not occur and PhN$_3$ which could be formed as a by-product in the main reaction, does not react with PhNCS.

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