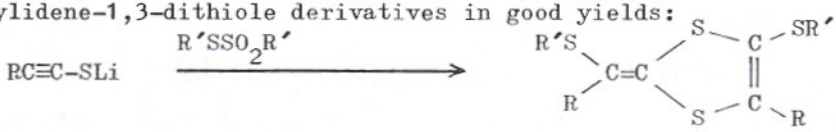
SYNTHESIS OF HETEROCYCLIC COMPOUNDS BASED ON ALKYNETHIOLATES.

R.S.Sukhai and L.Brandsma

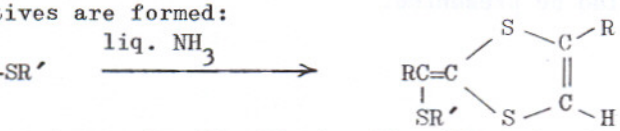
Department of Organic Chemistry of the University,
Croesestraat 79,3522 AD Utrecht,The Netherlands

Alkynethiolates, selenolates and tellurolates have been obtained for the first time in our laboratory from acetylides and the elements sulphur, selenium and tellurium respectively, in liquid ammonia. Of course they can also obtained in other organic solvents. Alkynethiolates are usefull intermediates for the synthesis of heterocycles. They can be considered as the anions of alkynethiols or the tautomeric thioketenes, a property reflected in the reactivity: $RC{\equiv}C^{\ominus} \xrightarrow{X_8} RC{\equiv}C{-}X^{\ominus} \leftrightarrow RC^{\ominus}{=}C{=}X$ (X= S)

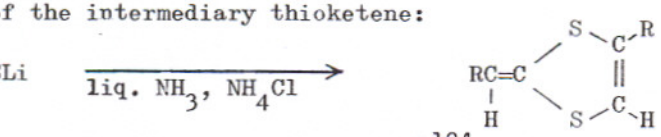
The ambident behaviour appears from the following reactions. Addition of thiosulfonates to an ethereal solution of an lithium alkynethiolate gives the 2-alkylidene-1,3-dithiole derivatives in good yields:



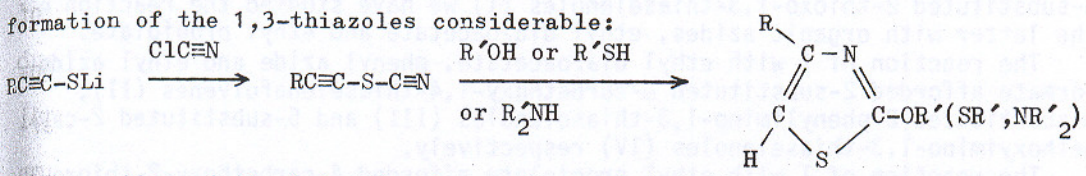
When acetylenic disulfides are dissolved in liquid ammonia, also 1,3-dithiole derivatives are formed:



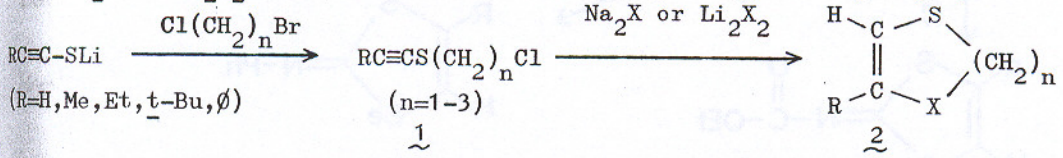
Addition of ammoniumchloride to alkynethiolates in liquid ammonia gives also the formation of 1,3-dithiole derivatives, which are formed by the dimerisation of the intermediary thioketene:



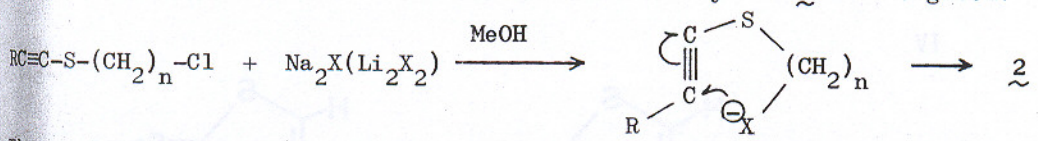
Alkynethiolates can also be applied in synthesis of a number of other types of heterocyclic compounds. For instance: When a ethereal solution of the lithium alkynethiolate is added to a solution of ClC≡N in ether, 1-alkynyl thiocyanates are formed in high yields. Reaction of the 1-alkynyl thiocyanates with alcohols, thiols and amines leads to the formation of 1,3-thiazole derivatives in good yields. Addition of $ZnCl_2$ appears to promote the formation of the 1,3-thiazoles considerable:



The formation of the 1,3-thiazole can be explained by assuming a nucleophilic attack of the alcohol,thiol or amine on the cyanide carbon atom,after which ring closure takes place by nucleophilic attack of nitrogen on the β-carbon atom.Another application of alkynethiolates for the synthesis of heterocycles is the reaction with $Cl(CH_2)_nBr$ which gives the 1-alkynethio-chloromethylene compounds(n=1) in good yields.Reaction of these acetylenic compounds 1 with Na_2X or Li_2X_2(X=S,Se,Te) gives the heterocycles 2 in very high yields:



The next mechanism for the formation of the heterocycles 2 can be given:



The nucleophile attacks the carbon-atom next to the Cl-atom,after which ring closure takes place by nucleophilic attack of $X^{\ominus}$ on the β-carbon atom, giving the heterocycles 2 after protonation.