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FUSED MESOIONIC HETEROCYCLES :

SYNTHESIS OF 1,2,4-TRIAZOLO(4,3-b)-1,2,4-TRIAZOLE DERIVATIVES

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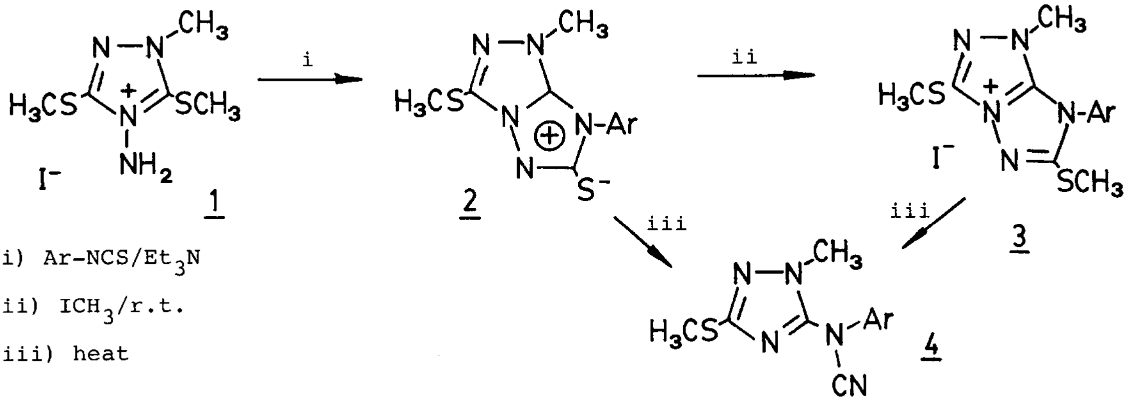
Summary: A number of mesoionic compounds derivatives of the bicyclic system 1,2,4-triazolo(4,3-b)-1,2,4-triazole have been prepared from 4-amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium iodide and aryl isothiocyanates.

Continuing our interest on the chemistry of fused mesoionic heterocycles[1] we have directed our attention to the preparation of mesoionic derivatives of the1,2,4-triazolo(4,3-b)-1,2,4-triazole ring system and we have already obtained some results in these series[2].We report here attempts to synthesize anhydro 7-aryl-6-mercapto-1,2,4-triazolo(4,3-b)-1,2,4-triazole hydroxides. 4-Amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium iodide (1),readily available from 4-amino-3,5-bis(methylthio)-1,2,4-triazole and methyl iodide[3],reacts with aryl isothiocyanates in dimethylformamide in the presence of triethylamine at room temperature to yield the new mesoionic compounds anhydro 7-aryl-1-methyl-3-methylthio-6-mercapto-1,2,4-triazolo(4,3-b)-1,2,4-triazole hydroxides (2) as crystalline solids in high yields (2; Ar=4-$CH_3.C_6H_4$; m.p. 157º; 78%). Compounds (2) react with methyl iodide in dry benzene at room temperature to give the corresponding methiodides (3) as crystalline solids in high yields (3; Ar=4-$CH_3.C_6H_5$; m.p. 165º; 81%).When compounds (2) or (3) are heated above their melting points under nitrogen for a short period of time are transformed into the monocyclic compounds (4) in excellent yields.However,the salts (3) reverted to the mesoionic products on heating in benzene.



i) Ar-NCS/Et_3N

ii) ICH_3/r.t.

iii) heat

Support for the formulation (2),(3) and (4) is clearly provided by their spectral data.The i.r. spectra of compounds (2) show absorption at 1370 cm^{-1} attributable to C=S stretching which may be compared in position with the thione stretching shown in the monocyclic anhydro 3-mercapto-1,2,4-triazolium hydroxides[4],while in compounds (3) this band is absent and compounds (4) show a strong absorption at 2248 cm^{-1} due to the cyano group stretching.In the ^{1}H-n.m.r. of (2),(3) and (4),the chemical shifts of $N-CH_3$ and $S-CH_3$ groups are characteristic at δ 3.4-3.7 and δ 2.7-2.8 respectively.Moreover,for (2 $Ar=C_6H_5$) the phenyl group appears as a singlet which is characteristic of a phenyl out-of-plane.The $N-CH_3$ and $S-CH_3$ groups carbons show up characteristically in the ^{13}C-n.m.r. spectra at 35.6-35.8 and 13.6-14.1 ppm respectively as do the cyano carbon group in (4) at 108.3-109 ppm while the C_6 in compounds (2) appears at 175.9 ppm and in compounds (3) at 162.3 ppm;the quaternary carbons C_3 and C_{7a} in (2) appear at 136.3 and 144.5 ppm respectively and in compounds (3) occur at 138.6 and 146.1 ppm respectively.The simple relationship between (2),(3) and (4) is shown by the appearance of the M^+ of (4) as the molecular ion in the mass spectra of (2) and (3),in addition the base peak of (3) corresponding to the fragment at m/e 142 (ICH_3).For all compounds peaks are also found at m/e Ar-NCN and at M^+-15.The elemental analyses of the new compounds are in good agreement with the proposed structures.

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