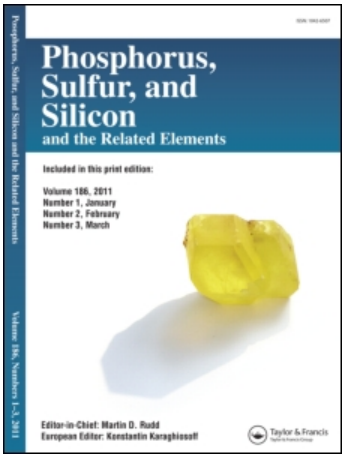

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SYNTHESIS OF FUSED HETEROCYCLES DERIVED FROM PERIMIDINES

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SYNTHESIS OF FUSED HETEROCYCLES DERIVED FROM PERIMIDINES

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The cyclocondensation of perimidine-2-thione **1** with propargyl bromide gave fused heterocycle **2**. The isomerization and aromatization of **2** in the presence of base afforded **4**.

Keywords: perimidine; Thiazole; propargyl bromide; exo methylene

The reactivity of thione heterocycles towards propargyl bromide has been studied and found to yield fused derivatives of thiazoles[1-8]. We report herein the use of perimidine-2-thione as a precursor for the synthesis of azole derivatives incorporating the perimidine moiety with anticipated biological activity.

Perimidine-2-thione synthetized in good yield from the reaction of 1,8-diaminonaphthalene with carbon disulfide, following a known procedure[9]. The reaction of **1** with propargyl bromide in refluxing EtOH in the presence of sodium acetate afforded a single compound. Analytical and spectroscopic data suggested that condensation and cyclization due to direct nucleophilic addition of amide to acetylene has occurred to give a cyclized compound containing exo methylene moiety **3**. The methylene thiazoline structure **3** was indicated by the presence of endocyclic (δ 3.9) and exocyclic (δ 4.9, J= 1.8 Hz; δ 5.6, J=1.8 Hz) methylene protons in ^{1}HNMR spectrum. The large difference in the ^{1}H chemical shifts of the deshielded resonance was assigned to the methylene proton *syn* to aromatic moiety.

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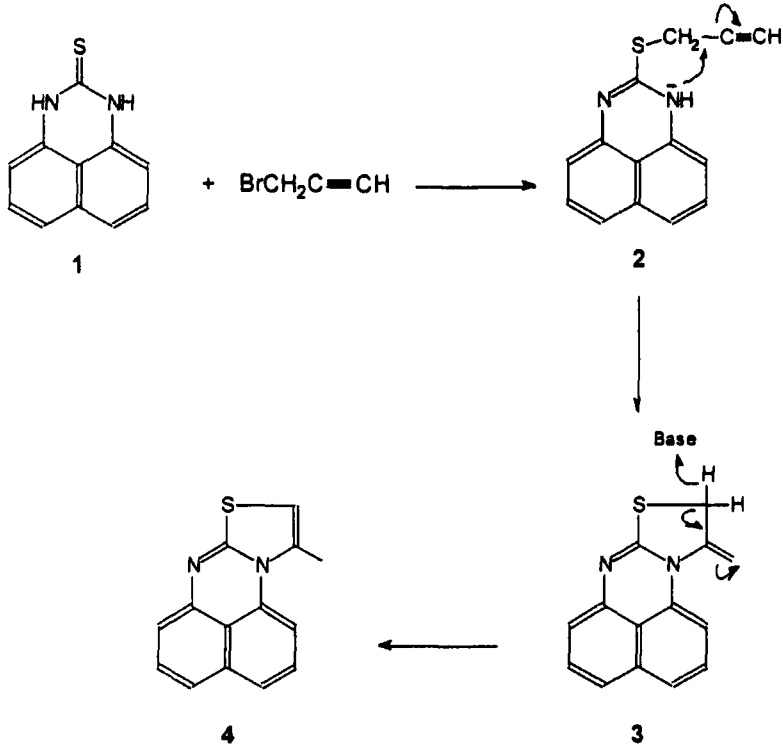
When **1** was refluxed with proargyl bromide in ethanol containing sodium acetate for a long period of time, a pure compound was isolated and identified as 9-methylthiazolo[3,2-a]perimidine **4**. 9-methylthiazolo[3,2-a]perimidine **3** can be converted to **4** by refluxing in EtOH in the presence of sodium acetate. For this cyclocondensation and isomerization the following mechanism can be written (Scheme).



1 2 3 4

SCHEME 1

EXPERIMENTAL SECTION

Mps were determined on a Reichert apparatus and are corrected. IR spectra were recorded on a Schimatzu spectrometer as KBr disc. ^{1}HNMR spectra were recorded on a Bruker (100 MHz) instrument. Mass spectra were obtained from Varian CH-7 at 70 eV.

PERIMIDINE-2-THIONE 1

1,8-Diaminonaphthalene (1.58 g, 0.01 mol) and carbon disulfide (1.2 g, 0.02 mol) were refluxed in EtOH (15 mL) for 15 min. The solution was cooled at room temperature and the precipitated solid was filtered and crystallized from ethanol to afford the title compound. Yield: 1.9 g (95%), mp: over 300°C, ^{1}HNMR δ (d_6-DMSO) 6.6 and 7.2 (m, 6H, aromatic protons), 11.4 (s, 2H, 2NH), IR, $\tilde{\nu}$ (KBr disc): 3200, 1625, 1020 cm^{-1}. Ms, m/z, M^+197.

9-METHYLENE-10H-THIAZOLO[3,2-a]PERIMIDINE 3

Compound 1 (0.2 g, 0.001 mol), sodium acetate (82 mg, 0.001 mol) and propargyl bromide (0.09 mL, 0.122 mg, 0.001 mol) were refluxed in absolute EtOH (20 mL) under on atmosphere of nitrogen for 5 hrs. The solvent was evaporated under reduced pressure and the crude product was directly subjected to column chromatography using $CHCl_3$:CH_2Cl_2(1:1) as eluent to obtain the title compound. Yield: 57%, mp: 203–5°C, ^{1}HNMR δ ($CDCl_3$): 3.9 (s, 2H, CH_2), 4.9 (d, J=1.8 Hz, 1H, =CH). 5.6 (d, J=1.8 Hz, 1H, =CH_2) 6.8, 7.3 (m, 6H, aromatic protons), IR, $\tilde{\nu}$ (KBr disc): 1620, 1570, 1490, 1440 cm^{-1}, Ms, m/z, M^+235

9-METHYL-THIAZOLO[3,2-a]PERIMIDINE 4

Compound **1** (0.2 g, 0.001 mol), sodium acetate (164 mg, 0.002 mol) and propargyl bromide (0.09 mL, 0.122 g, 0.001 mol) were refluxed in absolute EtOH under an atmosphere of nitrogen for 14 hrs. The solvent was evaporated under reduced pressure and the crude product was directly subjected to column chromatography using $CHCl_3$:CH_2Cl_2 (1:1) to afford the title compound. Yield: 48%, mp: 220–2°C, ^{1}HNMR δ ($CDCl_3$): 2.6 (d, 3H, CH_3), 6.7 (q, 1H, CH of thiazole). 6.9, 7.4(m, 6H, aromatic protons), IR, $\tilde{\nu}$ (KBr disc): 2940, 1430, 1375, 826, 760 cm^{-1}, Ms, m/z, M^+ 235

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