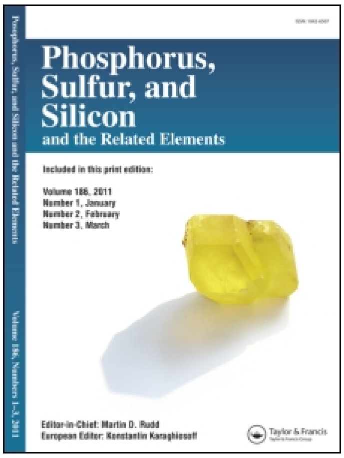

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A NOVEL DEPROPYNYLATIVE CYCLIZATION OF N-PROPYNYL-3-PROPYNYLTHIO-1,2,4-TRIAZIN-5-ONE

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A NOVEL DEPROPYNYLATIVE CYCLIZATION OF N-PROPYNYL-3-PROPYNYLTHIO-1,2,4-TRIAZIN-5-ONE

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6-Methyl-2N-propynyl-3-propynylthio-1,2,4-triazin-5-one and sodium methoxide were refluxed in N,N-diethylaniline to afford 3,6-dimethyl thiazolo [3,2-b] triazin-7-one.

Keywords: Thiazolo-triazine-7-one; Depropylation; Cope rearrangement; Claisen rearrangement

S→N Allylic rearrangement of allylthio pyrimidinone and allylthio −1,2,4-triazinone have been studied extensively owing to their synthetic utility[1,2]. Recently we have demonstrated the S→N propynylic rearrangement in 3-propynylthio-1,2,4-triazine **2**[3]. In continuation of our work in this area, we undertook a study of the rearrangement of 6-methyl-2N-propynyl-3-propynylthio-1,2,4-triazin-5-one **7** as it could undergo several interesting transformations described below.

It could lead to a 3,3-sigmatropic shift involving the propynylthioimidate and a type of aminopropynyl Claisen rearrangment in which the nitrogen of the propynylamino group is part of heterocyclic system. A second possibility is a diaza Cope rearrangment involving a N to N migration of the propynyl group followed by a propynyl thioimidate rearrangment. So far no such Cope rearrangment seems to have been reported in literature though a few examples of diazo cope rearrangment in acyclic system have been described[4–6]. Yet another interesting possibility is the synchronous

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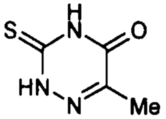
migration of the S-propynyl to N and N-propynyl to S, involving a ten membered transition state, simlar to that of the rearrangment of diaryloxy isobutylenes[7]. One more objective was to find out whether the above study would lead to simple methods of synthesis of annelated bicyclic or tricyclic heterocycles.

Available 6-methyl-1,2,4-triazine-3(2H)-thione-5(4H)-one **1** was caused to react with propynyl bromide in the presence of sodium methoxide to afford the corresponding 3-propynylthio derivative 2. We tried to condense the latter with one more propynyl group in the presence of bases such as sodium methoxide, triethylamine etc which led to the isolation of a mixtures of cyclized products **3–6** [8–11].

However when **1** was refluxed with excess of hexamethyl disilazane (HMDS) and a catalytic amount of $(NH_4)_2SO_4$ and propynyl bromide was added[12] after usual work up a single (TLC) compound was isolated in fairly good yield. This compoud was identified to be 6-methyl-2N-propynyl-3-propynylthio-1,2,4-triazin-5-one **7** by comparison of its UV spectrum with those of well established **5** (λmax, 280 nm)[8]and **6** (λmax 298 nm)[10]. 3,4-Disubstituted-1,2,4-triazin-5one are known to show the absorbtion maxima at the longer wavelengths compared with 2,3-disubstituted compounds[13].

When a solution of bis propynyl derivative **7** was refluxed in a mixture of sodium methoxide and N,N-diethylaniline for 4 hrs in a nitrogen atmosphere, a tarry solid was obtained which upon column chromatography over silica gel furnished a white solid (45%) m.p 224–225 °C. Analytical and spectral analysis indicated to be compound **5**. This was confirmed by comparing it with an authentic sample prepared according to the published procedures[7,9], When **7** was refluxed in toluene, aniline, HMPT or N,N-diethylaniline or in a sealed tube in toluene at 170 °C, only extensive polymerization was noticed though spots corresponding to **5**[8,9]and **8**[3] could be seen in TLC. There was very little reaction when **2** was refluxed in N,N-diethylaniline as seen from TLC.

Similarly heating of 2N-propynyl-1,2,4-triazine **9**[3] in a nitrogen atmosphere did not lead to a cyclized or depropynylated amine. 5-propynylthio-1,2,4-triazine **10**[14] was propynylated at N-2 by using HMDS to afford **11**. Neither cyclized nor depropynylated products could be detected when substitusted **11** (R=H or Me) was refluxed in a mixture of sodium methoxide and N,N-diethylaniline. On the basis of these findings we are postulating the following mechanism (Scheme 1).



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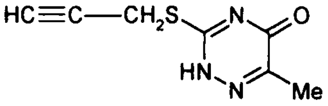

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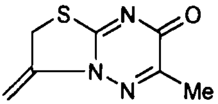

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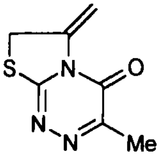

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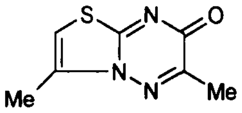

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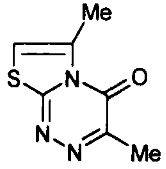

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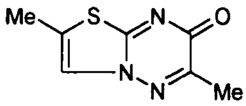
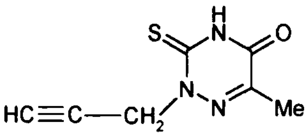


(8)



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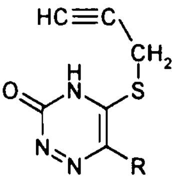

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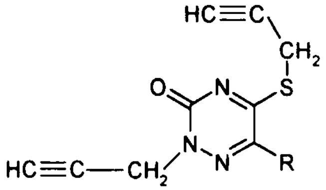
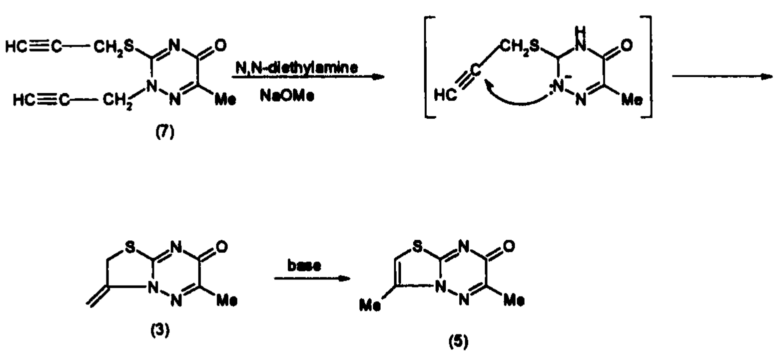


(11)

This mechanism involves the base promoted 5-exodiagonal cyclization[15], and depropynylation for aromatization[14].



SCHEME 1

EXPERIMENTAL

Melting points were obtained on a Büchi 530 and are uncorrected. ^{1}HNMR spectra were recorded on a Brucker AC 80 spectrometer, using TMS as an internal standard. IR spectra were recorded on a Perkin-Elemer model 883 using KBr disk and mass spectra on Fisson 800 Trio.

6-Methyl-2-N-propynyl-3-propynylthio-1,2,4-triazin-5-one(7)

Compound **2** (1.5g; 83 mmol) was refluxed in hexamethyldisilazane (HMDS) (3.5 ml excess) and a catalytic amount of $(NH_4)_2SO_4$ (60mg) was added until a clear solution was obtained. Excess HMDS was removed by distillation in vacuo. A catalytic amount of I_2 and propynyl bromide (0.80g, 5mmol) in CH_3CN (25ml) was added and the reaction mixture was refluxed for a further 5 hrs. After evaporation of the solvent in vacuo, the residue was treated with water to afford the product which was further purified by colum chromatography (eluent, petroleum ether: AcOEt /40:60). Yied (1.38g, 76%) mp 88–90 °C, ^{1}HNMR, ($CDCl_3$) 2.1 (t, 1.8 Hz, 1HC≡CH) 2.32(s,3H,Me) 2.56(t, 1.8Hz, 1HC≡CH),4.08 (d, 1.8Hz, SCH_2), 4.8(dl.8 Hz, N-CH_2), IR(KBr disk) 1648(C=O), 2122, 2974, 3269 cm^{-1}, UV λmax (EtOH), 238nm MS, m/z, M^+, 219(2),181(5),180(32),123(20),122(100),107(82),96(10),94(19),86(39),72 (1 0)71(27),69(35),54(30).

Depropynylative Cyclization of 7

Compound **7** (0.5g, 2.28 mmol) was dissolved in N,N-diethylaniline (10 ml) and to this solution sodium methoxide (0.123 g, 2.28 mmol) was added. The reaction mixture was refluxed for 4 hrs. After this period of time this solution was acidified by addition of hydrochloric acid (10 ml, 36%) and extracted by chloroform. The organic layer was dried over $MgSO_4$ and evaporated to dryness to give a residue which was directly subjected to column chromatography using petroleum ether: ethyl acetate 80:20 to give a compound which was identified to be 3,6-dimethyl thiazolo [3,2-b][1,2,4] triazin -7-one(5) Yield, 0.186g, 45%, mp 224–225°C (lit 226°C)[8], ^{1}HNMR, ($CDCl_3$), 2.4(s,6H,2CH_3), 6.5(s,1H, CH), IR(KBr disk) 1630 (amide carbonyl), 1422, 1367 cm^{-1}, MS, m/z, M^+, 181(2),178(73),174(36),150(9),137(100),108(9),68(40),67(40),43(9).

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