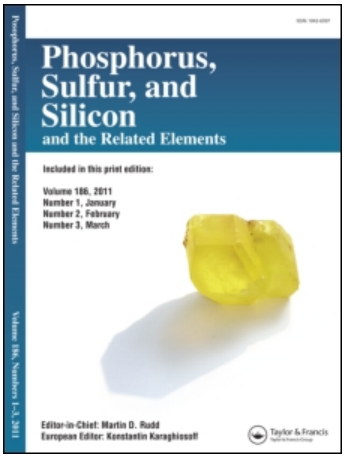

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REACTION OF DIMETHYL ACETYLENE-DICAROBXYLATE WITH TRIAZINONE

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The addition of dimethyl acetylenedicarboxylate (DMAD) to 6-menthy-1, 2,4-triazine-3(2H)thione-5(4H)-one afforded 2-methoxylcarboxy-7-methyl-1,3-thiazino[3,2-b][1,2,4]triazine-4,8-dione.

Acetylenic esters have proven to be very versatiale reagents for heterocyclization and many divers products can be prepared from the addition of this compounds to nitrogen and sulphur containing heterocycles[1].

As part of a research program on the synthesis of heterocyclic systems containing nitrogen and sulphur[2-6] and with a view of extending the synthetic utilliy of DMAD, we have investigated the addition of DMAD to 6-methyl-1,2,4-triazine-3(2H)-thione-5(4H)-one **1**. Compound **1** reacted with DMAD in acetonitrile to afford a single (tlc) compound. The IR spectrum showed two carbonyl absorptions but no NH bands. In the HNMR spectrum signals for one methyl group of the triazine ring at δ 2.27, one methyl group of ester at δ 3.84 and a vinyl proton at δ ca 7.28. were observed. The mass spectrum of this product showed low intensity (but observable) of the molecular ion peak corresponding to 1:1 molar adduct which condensed by MeOH elimination.

By the use of asymmetric triazine four cyclic structures (2a-d) are possible (Scheme 1.)

In 1978, Mc Killop and his co-Workers[7] reported that benzimidazole **3** reacted wich DMAD in either methanol or acetic acid to give mixtures of

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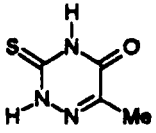

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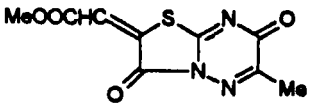
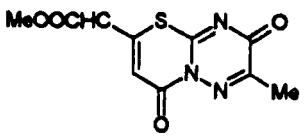


2a



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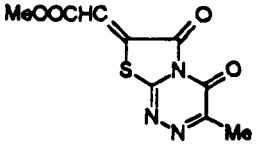
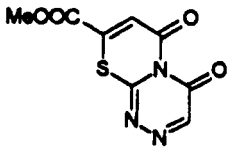


2c

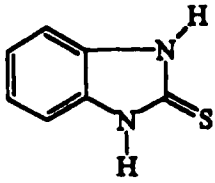


2d

SCHEME I

two 1:1 molar-MeOH adducts. One adduct was identified as 4 (by X-ray crystallography) but the other adduct which was not isolated was only tentatively assigned structure **5**. In 1981, Acheson et al[8] have found that the thione and DMAD reacted in wet or dry acetonitrile to give only 4 and in dry methanol to give only **5**.

For the compounds **4** and **5** the chemical shifts of the vinylic protons have been reported at δ 7.15 and 7.24 respectively. For distingiushing five (**2a,2c**) and six membered (**2b,2d**) adducts, we like to rely on Acheson finding[8]. The ^{1}HNMR spectra of our adduct showed a similar chemical shift at δ 7.28 as **6**. Moreover there is a marked differences of the chemical shifts of the carbon atoms in the ^{13}CNMR of five(**5**) and six(**6**) membered rings[8]. The proton decoupled ^{13}CNMR spectrum of our adduct showed the claimed close similarties in the resonance of the common carbon atoms of **6**. This comparison ruled out strutures (**2a** and **2c**).



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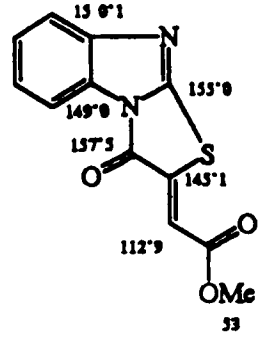

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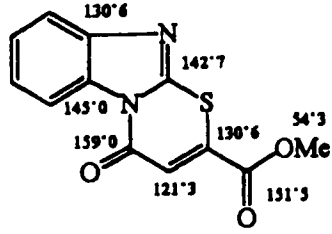
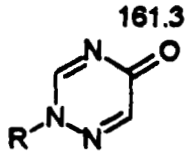


5

A part from vast literature[9] pointing out the reactivity of N2 of 1,2,4-triazine an immediate decision between structures **2b** and **2d** in favour of the former can be made by comparison of ^{13}C chemical shift of the adduct with those of similar compound having a 1,2,4-trazine nucleus. Daunis et al[10] have shown that in a 1,2,4-triazinone ring structure the chemical shift for the carbonyl carbon is makedly affected by the nature of the adjacent nitrogen. The reported chemical shift of 1,2,4-triazinone **6,7**[10] and **8,9**[11] are compared with that of our compound.

Since the values found for the cyclized product fit well with structure **2b**/our compound is identified as 2-methoxycarbonyl-7-methyl-1,3-thiazino [3,2-b][1,2,4]triazine-4,8-dione(Scheme 1.)



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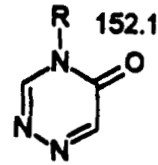

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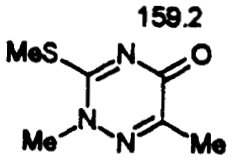

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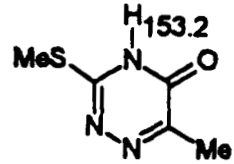

9

EXPERIMENTAL

2-Methoxycarbonyl-7methyl-1,3-thiazino[3,2-b][1,2,4] triazine-4,8-dione.2b

Compound **1** (1.43g, 0.01 mol) was dissolved in warm acetonitrile(25 ml). To this solution DMAD (0.012 mol) in acetonitrile (20 ml) was gently added. The mixtrue was stirred at room temperature for 1h and then set aside overnight during which time crystals separated. The crystalin compound was filtered off and recrystallized from EtOAc to afford the title compound, yield (70%) colourless crystals, mp 210–212, ^{1}HNMR, & (d_6-DMSO), 2.27 (s,3H,Me), 3.84(s,3H,CO_2Me), 7.28(s,1H,vinylic proton), ^{13}CNMR, & (d_6-DMSO), 17.4, 54.29, 121.36, 139.04, 153.27, 157.83, 163.84, 164.54 ppm. IR (KBr disc), 1701, 1759, 1595, 1560, cm^{-1}, M.S, m/z, M^+, 253.

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