(1) $X = CR_2$

(2) X = 0

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8π 1,3,4,5-Thiatriazines from Cycloadditions of Triazolium Imide 1,3-Dipoles with Methyl Cyanodithioformate

Richard N. Butler,* Paul D. O'Shea, D. Cunningham, and Patrick McArdle Chemistry Department, University College, Galway, Ireland

(5)

A high-yield route to 2,4,6-trisubstituted 1,3,4,5-thiatriazines is described along with an X-ray crystal structure of the ring system

The monocyclic higher azines represent classes of compounds which are exceptionally rare¹ and even for the simpler 1,2,3-triazines (1) there are relatively few synthetic routes and few

cyanodithioformate \dagger (7)⁶ in benzene at ambient temperatures gave high yields of the new compounds (4) in a particularly easy reaction (Table). By analogy with the routes^{2,3} to compounds (2) and (3) we

Treatment of the triazolium imide 1,3-dipoles (6) with methyl

suggest that compounds (4) are formed via the sequence of intermediates (8)—(10) (Scheme). None of these could be isolated directly or detected owing to the rapidity of the reaction of (6) and (7) to give (4). The fragment eliminated in the step (9) to (10) was detected only as a small quantity of resin. It may have been derived from the imine MeS(CN)C=NPH since no methyl sulphide was detected during the reaction. When an attempt was made to intercept the intermediate (10) by blocking



Scheme. *13C N.m.r. shift in CDCl₃ shown

examples of monocyclic compounds.¹ The rings (2)^{2,3} and (3),⁴ which are 8π six-atom heterocycles, were unknown until recently.²⁻⁴ We report a new route to the sulphur analogue of these 8π higher azine systems, the monocyclic 1,3,4,5-thiatriazine derivatives (4). There is only one previous report ⁵ of this ring system. The oxidised form (5) was obtained in low yield among the products of the reaction of substituted thiirene 1,1-dioxides with azide ion. The oxidised form of the ring was labile to loss of SO₂ and the reduced parent ring is unknown.



† While compound (7) has been used as a dienophile, as far as we are aware this is its first use as a dipolarophile in which role it is highly effective. It also gave high yields of the dihydrothiadiazoles (A) when treated with benzonitrile N-p-nitrophenylimide.

Table. Products from (6) and (7) in benzene at ambient temperat
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Compd.	R,R	Ar	M.p. (°C)	Yield (%)
(4 a)	Ph	Ph	111—113"	84
(4b)	Ph	p-BrC ₆ H ₄	145—146 ^{<i>b</i>}	91
(4c)	Ph	p-NO ₂ C ₆ H ₄	1 92—193 °	86
(11)	$(CH_2)_4$	$p-NO_2C_6H_4$	204—206 ^{<i>b</i>}	85

" From MeOH. b From EtOH. From PrOH.



Figure. X-Ray crystal structure of compound (4a)

the disrotatory outward ring expansion to (4) by linking the bridgehead substituents using the substrate [6; RR = $(CH_2)_4$] the product of the reaction of (6) and (7) was the triazole (11) (Table). Since compound [6; RR = (CH_4) , Ar = p-NO₂C₆H₄] is stable for prolonged periods in benzene at 25 °C the triazole (11) was formed during the reaction, probably arising by loss of S from the intermediate [10; RR = $(CH_2)_4$].

The X-ray crystal structure of compound (4a) (Figure) shows a boat-shaped 1,3,4,5-thiatriazine ring with equatorial substituents. The C-S-C bond angle at 93.4° is similar to that in thiophene (92.2°) and hydrogen sulphide (92.1 \pm 0.2°). The C-S bond length at 1.783 Å is longer than the normal C(sp²)-S (divalent) distance of 1.751 Å⁷ and shorter than the single C-S bond length (1.82 \pm 0.1) of dimethyl sulphide suggesting some conjugation. The ring may thus be viewed as composed of two isolated planar thiohydrazine units with the 1-S and 4-N atoms common and this necessitates a boat structure. Models show that a chair structure would result in severe loss of planarity in the thiohydrazidine units.

Experimental

The cycloadditions were particularly facile. The following is a typical example. Methyl cyanodithioformate $(7)^{6}$ (379 mg, 3.24

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mmol) in dry benzene (50 ml) was added to bisphenylazostilbene (1.26 g, 3.24 mmol) [which reacts as (**6a**)] and the solution was stirred for 1 h at ambient temperature. It was then evaporated under reduced pressure and the residue was stirred in cold ethanol (10 ml) to give crystals of compound (**4a**). These were collected and recrystallised from methanol, m.p. 111–113 °C (from MeOH) (84%) (Found: C, 72.7; H, 4.7; N, 12.5. $C_{20}H_{15}N_3S$ requires C, 72.9; H, 4.5; N, 12.7%); $\delta_H(CDCl_3)$ (Ar signals only) 7.15 (t, 1 H), 7.40–7.45 (m, 8 H), 7.8 (d, 2 H), and 8.0–8.03 (m, 4 H); $\delta_C(CDCl_3)$ 140.1 (C=N), 133.6, 130.9, 128.7, 127.2 (2-Ph), 148.4, 130.9, 123.9, and 117.0 (4-Ph).

Crystal data for $C_{20}H_{15}N_3S$ (4a). Monoclinic, a = 8.041(a), b = 18.813(7), c = 10.884(2) Å; Z = 4; space group $P2_{1/a}$; 1 045 reflections observed with $I > 3\sigma I$ using a CAD4 diffractometer and Mo- K_a radiation; $2\theta_{max.} = 48^\circ$. The structure was solved by direct methods, SHELX 86⁸ and refined with 127 variable parameters using SHELX 76.⁹ After full matrix refinement; R = 5.76 and $R_w = 6.62\%$. The maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.13 and -0.14 e/Å^{10} The ORTEP program was used to obtain the drawings.¹⁰ Atomic co-ordinates and bond lengths and angles have been deposited at the Cambridge Crystallography Data Centre [see Notice to Authors (1989), J. Chem. Soc., Perkin Trans. 1, 1989, Issue 1].

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