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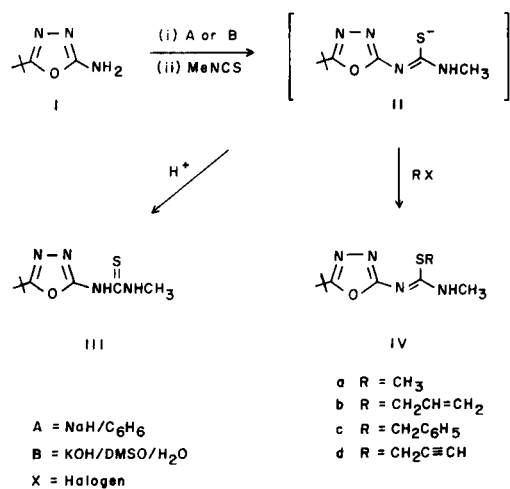
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Procedures are described for converting 2-amino-1,3,4-oxa- and thiadiazoles into various products in one-pot syntheses. The preparative method employs alkali metal derivatives of the heterocyclic amines as the reactive species.

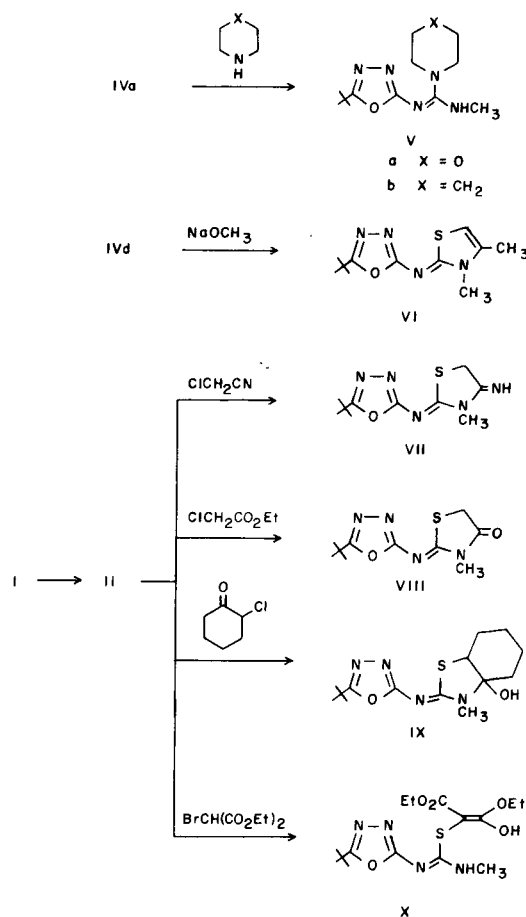
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During the course of our work on biologically-active heterocycles, we investigated the synthetic utility of 2-amino-1,3,4-oxa- and thiadiazoles. Despite reports of the preparation of 2-thioureido-1,3,4-oxadiazoles from 2-amino-1,3,4-oxadiazoles and isothiocyanates [1,2], our initial studies indicated that the 2-thioureido analogue III was not readily obtained from the reaction of 2-amino-5-*t*-butyl-1,3,4-oxadiazole (I) and methyl isothiocyanate. However, if I was first converted to a sodium salt prior to the reaction with the isothiocyanate, a high yield of III ensued. Subsequent investigations have shown that alkali metal derivatives of the heterocyclic amines undergo a variety of reactions which would not be expected of the unmodified amines. We now wish to describe this work.



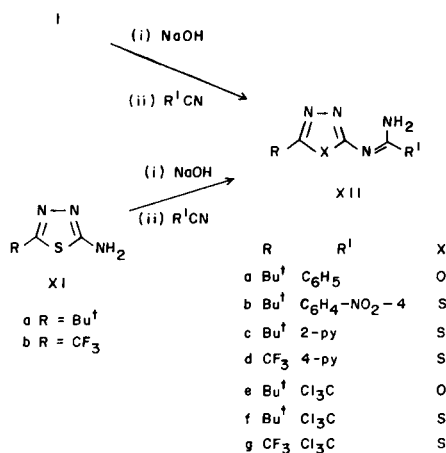
Sodium hydride has been used to generate a sodio derivative of 2-amino-4-methoxy-6-methyltriazine for reaction with a carbonimidodithioate to provide an *N*-(4-methoxy-6-methyltriazin-2-yl)isothiourea [3]. We prepared the thiourea III under similar conditions by treating a suspension of I in benzene with sodium hydride followed by methyl isothiocyanate. After neutralising the intermediate isothioironium salt II an 87% yield of III was obtained. The reaction could also be performed in an aqueous medium and was most conveniently carried out in a solution of dimethylsulphoxide and water using potassium hydroxide as the base.

A number of structures were accessible *via* alkylation of II. The isothiureas IVa,b,c and d were prepared in this way. Morpholine and piperidine reacted with IVa affording the corresponding guanidines Va and Vb. Under basic conditions IVd cyclised to the thiazoline VI whereas ring closure occurred *in situ* during alkylations with chloroacetonitrile, ethyl chloroacetate and 2-chlorocyclohexanone to provide the imino-, oxo- and hydroxythiazolidines VII, VIII and IX respectively [4]. Surprisingly, alkylation with diethyl bromomalonate was not accompanied by cyclisation. The product from this reaction is assigned the hydroxy structure X on the basis of its ¹H nmr spectrum which showed two broad downfield signals each inte-

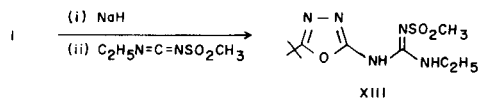


grating for an exchangeable proton (OH and NHCH_3) and an absorption at 3370 cm^{-1} in the ir (OH stretching) which was not present in the spectra of the other isothioureas.

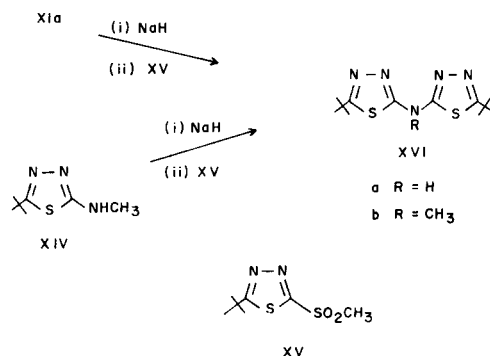
Reactions of 2-amino-1,3,4-oxadiazoles with dicyandiamide at elevated temperatures are reported to give 1,3,4-oxadiazol-2-ylbiguanides [5]. In the present study, related reactions under milder conditions were conducted between nitriles and the sodium salts of I and the 2-amino-1,3,4-thiadiazoles XIa and XIb. Amidines were produced in yields which were broadly consistent with the reactivities of the nitriles. A low conversion to the benzamidine XIIa occurred with benzonitrile but the more electron-deficient cyano groups in *p*-nitrobenzonitrile, 2- and 4-cyanopyridines and trichloroacetonitrile furnished higher yields of the respective analogues XIIb, XIIc, XII d and XIIe,f,g.



In a similar synthesis the tri-substituted guanidine XIII was prepared from the sodio derivative of I and *N*-ethyl-*N'*-methanesulphonylcarbodiimide.



In view of the aforementioned addition reactions it was not unexpected to find that the alkali metal derivatives entered into displacements. The sodium salts of XIa and the methylamino analogue XIV both coupled to a second thiadiazole ring in reactions with 2-methanesulphonyl-5-*t*-butyl-1,3,4-thiadiazole (XV). The ¹H nmr data supported the assignment of the *bis* structures XVIa and XVIb to the corresponding products. The spectrum of each compound showed only one signal for the *t*-butyl groups [6]. The structural symmetry of XVIa and XVIb is indicative of displacement of the methanesulphonyl group by the exocyclic nitrogen atoms of the amine salts.



EXPERIMENTAL

Melting points are uncorrected. The ir spectra were determined on a Pye Unicam SP 1100 spectrophotometer using potassium chloride discs. The ¹H nmr spectra were determined on a Perkin-Elmer R-32. Chemical shifts are reported on the δ scale using TMS as an internal standard. Elemental analyses were performed on a Carlo Erba Elemental Analyser Model 1102.

1-(5-*t*-Butyl-1,3,4-oxadiazol-2-yl)-3-methylthiourea (III).

Method a.

To a suspension of 7.05 g (0.05 mole) of 2-amino-5-*t*-butyl-1,3,4-oxadiazole (I) stirred in 150 ml of dry benzene was added 2.40 g (0.05 mole) of sodium hydride (50% dispersion in oil) which had been pre-washed with hexane. The reaction mixture was stirred at room temperature over night and then treated with 3.65 g (0.05 mole) of methyl isothiocyanate and refluxed for 3 hours. The suspension was cooled to room temperature and then mixed with water until all solid material had dissolved. The aqueous phase was separated and acidified with concentrated hydrochloric acid. The product was filtered, washed with water and dried. Recrystallisation from benzene/60-80 petroleum ether gave 8.0 g (87%) of pure material, mp 154-156°; ir: ν NH 3250 (b) cm^{-1} ; ¹H nmr (DMSO-*d*₆): δ 1.36 (s, 9H), 3.14 (d, 3H, collapses to singlet on addition of deuterium oxide), 9.56 (b, 1H, exchanges with deuterium oxide), 11.95 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for C₈H₁₄N₄OS: C, 44.84; H, 6.59; N, 26.15. Found: C, 45.22; H, 6.48; N, 25.96.

Method b.

To a stirred solution of 14.10 g (0.1 mole) of the amine (I) in 100 ml of dimethylsulphoxide was added a solution of 5.60 g (0.1 mole) of potassium hydroxide in 10 ml of water. After a few minutes 7.30 g (0.1 mole) of methyl isothiocyanate was added and stirring was continued for a further 10 minutes. The mixture was diluted with water. The aqueous solution was acidified whereupon the product separated as a solid. The solid was filtered, washed with water, dried and recrystallised from isopropanol/hexane as white prisms, yield 11.0 g (51%), mp 153-155°.

Synthesis of the Isothioureas IVb,c and d and the Thiazolidines VII and IX.

General Procedure.

To a stirred suspension of 2.82 g (0.02 mole) of I in 50 ml of dry benzene was added 0.96 g (0.02 mole) of sodium hydride (50% dispersion in oil). The mixture was stirred and refluxed for 1 hour. After cooling to room temperature the mixture was treated with 1.46 g (0.02 mole) of methyl isothiocyanate and then refluxed for a further 1 hour. To the reaction mixture at room temperature was added 0.02 mole of the alkyl halide. Refluxing was resumed for a further 2½ hours. The benzene solution was washed with water, dried over magnesium sulphate and evaporated to dryness under vacuum. The solid residue recrystallised from an appropriate solvent.

The S-allyl derivative IVb was obtained from allyl bromide in 54% yield and recrystallised from 40-60 petroleum ether, mp 112-113°; ν NH 3210 (b), 3110 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.25 (s, 9H), 2.92 (d, 3H, collapses to a singlet on addition of deuterium oxide), 3.62-3.83 (m, 2H), 4.95-5.35 (m, 2H), 5.60-6.05 (m, 1H), 9.0 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{N}_4\text{OS}$: C, 51.94; H, 7.13; N, 22.03. Found: C, 51.50; H, 7.32; N, 22.21.

The S-benzyl derivative IVc was prepared in 54% yield from benzyl bromide and recrystallised from 40-60 petroleum ether, mp 84-85°; ν NH 3200 (b), 3140 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.37 (s, 9H), 2.92 (d, 3H, collapses to a singlet on addition of deuterium oxide), 4.33 (s, 2H), 7.12-7.46 (m, 5H), 9.05 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_4\text{OS}$: C, 59.18; H, 6.62; N, 18.41. Found: C, 59.09; H, 6.88; N, 18.48.

The S-propargyl derivative IVd was obtained from propargyl bromide in 52% yield and recrystallised from hexane, mp 105-107°; ν NH 3250 (b), 3120 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.30 (s, 9H), 2.95 (d, 3H, collapses to a singlet on addition of deuterium oxide), 3.08 (m, 1H), 3.94 (d, 2H), 9.10 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_4\text{OS}$: C, 52.36; H, 6.39; N, 22.21. Found: C, 51.94; H, 6.51; N, 21.93.

The imine VII was prepared in 53% yield from chloroacetonitrile and recrystallised from acetonitrile, mp 180-182° (d); ν NH 3215, C=N 1670 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.36 (s, 9H), 3.32 (s, 3H), 4.04 (s, 2H), 7.20-7.80 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{N}_4\text{OS}$: C, 47.41; H, 5.97; N, 27.65. Found: C, 46.99; H, 5.99; N, 27.40.

The hydroxy derivative IX was prepared in 40% yield from 2-chloro-cyclohexanone and recrystallised from acetonitrile, mp 163-165°; ν OH 3120 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.24 (s, 9H), 1.24-2.15 (m, 8H), 2.85 (s, 3H), 3.45 (t, 1H), 6.27 (s, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$: C, 54.17; H, 7.14; N, 18.05. Found: C, 54.45; H, 7.41; N, 18.39.

Synthesis of the Isothioureas IVa and X, and the Thiazolidine VIII.

General Procedure.

A solution of 2.82 g (0.02 mole) of I in 20 ml of DMSO was stirred and cooled in ice-water and treated with a solution of 1.12 g (0.02 mole) of potassium hydroxide in 5 ml of water followed by 1.46 g (0.02 mole) of methyl isothiocyanate. After 10 minutes, 0.02 mole of the appropriate alkyl halide was added and stirring was continued for another 10 minutes. The reaction mixture was diluted with water and the product was taken up in dichloromethane. The organic solution was dried over magnesium sulphate and evaporated under vacuum. The residual material recrystallised from an appropriate solvent.

The isothiourea IVa was prepared in 68% yield from methyl iodide and recrystallised from 40-60 petroleum ether, mp 100-101°; ν NH 3225 (b), 3130 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.27 (s, 9H), 2.40 (s, 3H), 2.95 (d, 3H, collapses to a singlet on addition of deuterium oxide), 9.05 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{N}_4\text{OS}$: C, 47.34; H, 7.06; N, 24.54. Found: C, 47.60; H, 7.25; N, 24.33.

The hydroxy ester X was obtained in 13% yield from diethyl bromomalonate and recrystallised from acetonitrile, mp 214-216°; ν OH 3370, NH, 3230 (b), 3150 (b), C=O 1735 cm^{-1} ; ^1H nmr (DMSO- d_6): 1.16-1.32 (s, t, 15H), 3.00 (d, 3H, collapses to a singlet on addition of deuterium oxide), 4.25 (q, 4H), 8.50 (b, 1H, exchanges with deuterium oxide), 9.45 (s, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$: C, 48.37; H, 6.5; N, 15.04. Found: C, 48.60; H, 6.40; N, 15.00.

The oxo derivative VIII was prepared from ethyl chloroacetate in 48% yield and recrystallised from ethyl acetate, mp 174-175°; ν C=O 1730 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.37 (s, 9H), 3.29 (s, 3H), 3.96 (s, 2H).

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$: C, 47.23; H, 5.55; N, 22.03. Found: C, 47.40; H, 5.50; N, 22.23.

Synthesis of the Guanidines Va and Vb.

N'-(5-*t*-Butyl-1,3,4-oxadiazol-2-yl)-*N*-methyl-4-morpholinecarboximidamide (Va) was prepared in 37% yield by gently refluxing a solution of 0.57 g (2.5 mmoles) of IVa in 2 ml of morpholine for 7 hours. The excess amine was removed under vacuum and the residual solid recrystallised from benzene/60-80 petroleum ether, mp 160-161°; ν NH 3220 (b), 3100 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.21 (s, 9H), 2.75 (d, 3H, collapses to a singlet on addition of deuterium oxide), 3.15-3.35 (m, 4H), 3.45-3.65 (m, 4H), 7.70 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{N}_5\text{O}_2$: C, 53.92; H, 7.92; N, 26.20. Found: C, 54.22; H, 8.06; N, 26.31.

The analogue Vb was prepared in the same way from piperidine and recrystallised from benzene/60-80 petroleum ether in 45% yield, mp 115-116°; ν NH 3220 (b), 3110 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.24 (s, 9H), 1.35-1.60 (m, 6H), 2.72 (d, 3H, collapses to a singlet on addition of deuterium oxide), 3.05-3.35 (m, 4H), 7.60 (b, 1H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{N}_5\text{O}$: C, 58.84; H, 8.74; N, 26.40. Found: C, 58.64; H, 8.99; N, 26.10.

2-[(5-*t*-Butyl-1,3,4-oxadiazol-2-yl)imino]-2,3-dihydro-3,4-dimethylthiazole (VI).

A mixture of 5.0 g of IVd, 0.5 g of sodium methoxide and 50 ml of methanol was refluxed for 2 hours. The solvent was distilled off under vacuum and the residue was triturated with water. The resulting solid was filtered and dried. It was dissolved in hot isopropanol, treated with activated charcoal, filtered and diluted with 40-60 petroleum ether. The product crystallised from the refrigerated solution as white flakes, yield 3.0 g (60%), mp 136-138°; ^1H nmr (DMSO- d_6): δ 1.25 (s, 9H), 2.16 (bs, 3H), 3.40 (s, 3H), 6.46 (bs, 1H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_4\text{OS}$: C, 52.36; H, 6.39; N, 22.21. Found: C, 52.00; H, 6.40; N, 21.87.

General Procedure for the Synthesis of the Guanidines XIIa-g.

A solution of 0.02 mole of the heterocyclic amine in 20-30 ml of DMSO was treated with a solution of 2.0 ml of 40% aqueous sodium hydroxide followed after a few minutes by 0.02 mole of the nitrile. In the synthesis of XIIa the reaction mixture was stirred for 1 hour at room temperature and then at 60° for 1 hour. In other cases the reactants were stirred together for 1 hour at room temperature. Products were isolated by diluting the reaction mixture with water, filtering off the solid and recrystallising from an appropriate solvent.

The benzamidine XIIa was prepared from benzonitrile and I in 16% yield. Recrystallisation from benzene/60-80 petroleum ether gave mp 187°; ν NH 3300 (b), 3150 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.29 (s, 9H), 7.35-7.55 (m, 3H), 7.92-8.10 (m, 2H), 9.00 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}$: C, 63.91; H, 6.60; N, 22.94. Found: C, 64.27; H, 6.73; N, 22.68.

The *p*-nitrobenzamidine XIIb was prepared from XIa and *p*-nitrobenzonitrile. After recrystallisation from benzene/60-80 petroleum ether the yield was 55%, mp 203°; ν NH 3350-3100 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.40 (s, 9H), 8.20-8.40 (m, 4H), 9.40 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_5\text{O}_2\text{S}$: C, 51.13; H, 4.95; N, 22.94. Found: C, 51.30; H, 5.09; N, 22.97.

The 2-pyridylamidinium XIIc was prepared in 77% yield from XIa and 2-cyanopyridine. Recrystallisation from acetonitrile gave mp 98-100°; ν NH 3250-3360 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 1.41 (s, 9H), 7.50-7.70 (m, 1H), 7.85-8.20 (m, 1H), 8.25-8.40 (m, 1H), 8.63-8.75 (m, 1H), 9.15 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_5\text{S}$: C, 55.15; H, 5.79; N, 26.80. Found: C, 55.41; H, 5.80; N, 26.93.

The 4-pyridylamidinium XIIId was prepared from XIb and 4-cyanopyridine in 62% yield. After recrystallisation from acetonitrile the product had mp 171-172°; ν NH 3330 (b) cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.92-8.06

(m, 2H), 8.72-8.90 (m, 2H), 9.57 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $C_9H_8F_3N_5S$: C, 39.56; H, 2.21; N, 25.63. Found: C, 39.34; H, 2.03; N, 25.93.

The trichloromethylamidinium XIIe was prepared from I and trichloroacetonitrile. After recrystallisation from isopropanol the yield was 54%, mp 169-170°; ir: ν NH 3350 (b) cm^{-1} ; 1H nmr (DMSO- d_6): δ 1.25 (s, 9H), 9.15 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $C_9H_7Cl_3N_4O$: C, 33.64; H, 3.88; N, 19.62. Found: C, 33.31; H, 3.64; N, 19.35.

The trichloromethylamidinium XIIIf was prepared from XIa and trichloroacetonitrile in 67% yield. After recrystallisation from acetonitrile the product had mp 159-160°; ir: ν NH 3340 (b) cm^{-1} ; 1H nmr (DMSO- d_6): δ 1.37 (s, 9H), 9.28 (b, 2H, exchanges with deuterium oxide).

Anal. Calcd. for $C_9H_7Cl_3N_4S$: C, 31.85; H, 3.68; N, 18.58. Found: C, 31.55; H, 3.82; N, 18.29.

The trichloromethylamidinium XIIg was prepared from XIb and trichloroacetonitrile. After recrystallisation from 80-100 petroleum ether the yield was 53%, mp 105-106°; ir: ν NH 3160-3320 cm^{-1} ; 1H nmr (DMSO- d_6): δ 9.50 (b, exchanges with deuterium oxide).

Anal. Calcd. for $C_9H_7Cl_3F_3N_4S$: C, 19.15; H, 0.64; N, 17.87. Found: C, 19.45; H, 0.53; N, 17.95.

N[[[5-*t*-Butyl-1,3,4-oxadiazol-2-yl]amino][ethylamino]methylene]methanesulphonamide (XIII).

A mixture of 1.41 g (0.01 mole) of I, 0.48 g (0.01 mole) of sodium hydride (50% dispersion in oil) and 30 ml of benzene was boiled under reflux for 1 hour. It was then treated with 1.48 g (0.01 mole) of *N*-ethyl-*N'*-methanesulphonylcarbodiimide [7] and refluxing was resumed for a further 5 hours. The organic solution was thoroughly mixed with water. The aqueous phase was separated and neutralised by the addition of concentrated hydrochloric acid. The product was filtered, washed with a small amount of water, dried and recrystallised from benzene/60-80 petroleum ether, yield 1.1 g (38%), mp 124-125°; ir: ν NH 3330 (b), 3170 (b) cm^{-1} ; 1H nmr (DMSO- d_6): δ 1.21 (t, 3H), 1.42 (s, 9H), 3.12 (s, 3H), 3.45 (m, 2H, becomes a quartet on addition of deuterium oxide), c. 8-9 (b, 2H, exchanges on addition of deuterium oxide).

Anal. Calcd. for $C_{10}H_{19}N_5O_3S$: C, 41.51; H, 6.62; N, 24.21. Found: C, 41.80; H, 6.53; N, 23.97.

2-*t*-Butyl-5-methanesulphonyl-1,3,4-thiadiazole (XV).

Prepared by a method previously reported for other 2-substituted analogues [8]. Methyl *N'*-pivaloylcarbodiimide was prepared by the dropwise addition of 147.0 ml of carbon disulphide to a stirred solution of 147.0 g of pivaloylhydrazine and 73.4 g of potassium hydroxide in 800 ml of ethanol. The reaction mixture was stirred at 5° and treated dropwise with 162.0 g of methyl iodide. After 2 hours the mixture was added to 5 litres of ice-water. The product was filtered and dried giving a crude yield of 176.4 g (78%). 2-*t*-Butyl-5-methylmercapto-1,3,4-thiadiazole was prepared by adding the dithiocarbamate protonwise to 460 ml of concentrated sulphuric acid stirred at room temperature. The resulting solution was kept overnight and then poured carefully onto ice-water. The product separated as an orange oil which was extracted into dichloromethane. The dried extracts were evaporated under vacuum to remove solvent. The residual oil weighed 160.0 g (86% yield); 1H nmr (deuteriochloroform): δ 1.45 (s, 9H), 2.74 (s, 3H). To a stirred solution of 9.5 g of the sulphide in 75 ml of acetic acid was added dropwise a solution of 16.8 g of potassium permanganate in 250 ml of water. The reaction mixture was stirred for 3 hours after the addition. Sulphur dioxide was then passed through it until the colour was discharged. The solid was filtered, washed with water, dried and recrystallised from isopropanol/60-80 petroleum ether giving 6.5 g (58%) of 2-*t*-butyl-5-methanesulphonyl-1,3,4-

thiadiazole as colourless prisms, mp 118-120°; 1H nmr (DMSO- d_6): δ 1.50 (s, 9H), 3.62 (s, 3H).

Anal. Calcd. for $C_9H_{11}N_2O_2S_2$: C, 38.16; H, 5.49; N, 12.72. Found: C, 37.83; H, 5.56; N, 12.79.

Bis(5-*t*-butyl-1,3,4-thiadiazol-2-yl)amine (XVIa).

To a stirred suspension of 7.85 g (0.05 mole) of XIa in 40 ml of dry dimethoxyethane was added 2.40 g (0.05 mole) of sodium hydride (50% dispersion in oil). After the initially vigorous effervescence had ceased (approximately 30 minutes) the solution was cooled in ice-water and treated with 11.00 g (0.05 mole) of XV. The mixture was stirred for 3 hours at room temperature and then concentrated to a small volume under vacuum. The residual material was dissolved in 50 ml of water and acidified. The white precipitate was filtered and dried. After washing with 60-80 petroleum ether, the solid crystallised from acetonitrile as colourless needles, yield 4.2 g, 28%, mp 181-183°; ir: ν NH 2500-2850 cm^{-1} ; 1H nmr (DMSO- d_6): δ 1.36 (s).

Anal. Calcd. for $C_{12}H_{19}N_5S_2$: C, 48.45; H, 6.44; N, 23.55. Found: C, 48.32; H, 6.68; N, 23.20.

N,N-Bis(5-*t*-butyl-1,3,4-thiadiazol-2-yl)methylamine (XVIb).

A stirred solution of 1.71 g (0.01 mole) of XIV in 25 ml of dry benzene was treated with 0.48 g (0.01 mole) of sodium hydride (50% dispersion in oil). After effervescence had ceased (approximately 4 hours) 2.20 g (0.01 mole) of XV was added and stirring was continued for a further 4 hours. The reaction mixture was then added to water and shaken thoroughly. The organic layer was separated, dried over magnesium sulphate and evaporated to dryness under vacuum. The residual crystalline solid recrystallised as colourless flakes from 2-propanol, yield 2.3 g (74%), mp 138-140°; 1H nmr (DMSO- d_6): δ 1.41 (s, 18H), 3.79 (s, 3H).

Anal. Calcd. for $C_{13}H_{21}N_5S_2$: C, 50.13; H, 6.80; N, 22.49. Found: C, 50.51; H, 7.08; N, 22.73.

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