Nucleophilic Behaviour of Enamines Derived from 2-Methyl-5,6-dihydro-2*H*-thiopyran-3(4*H*)-one 1,1-Dioxide

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The reactivity of the title compounds towards some electrophiles is investigated. An interesting ring-enlargement product is isolated in the reaction of 3-pyrrolidin-1-yl-5,6-dihydro-4*H*-thiopyran 1,1-dioxide with methanesulphonyl chloride.

In continuation of our studies on the structures and reactivities of vinylogous sulphonamides,[1] we have prepared the system 2-methyl-5,6-dihydro-2*H*-thiopyran-3(4*H*)-one 1,1-dioxide (1),[1,2] from which the corresponding morpholino and pyrrolidinyl enamines, (2) and (3) respectively, have been synthesized (Scheme 1). Both enamines are single isomers, but while compound (2) is a simple enamine, (3) is a vinylogous sulphonamide. Their different structures are also reflected in the values of the related spectroscopic parameters (Table).

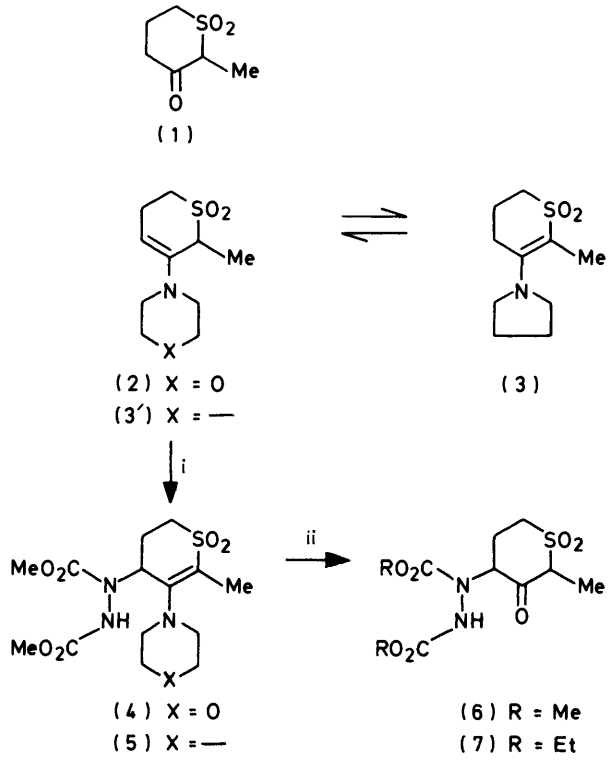
A comparison with the systems bearing no methyl group at C-2,[1] both of which are Δ^2-isomers, suggests that steric effects are the dominant factor in the morpholino derivative. This is in contrast with the results obtained by Gurowitz [3] for the corresponding systems derived from 2-methylcyclohexanone, in which the steric interaction between the base and the methyl group was stronger in the pyrrolidinyl system than in the morpholino one. In the former in fact the tetrasubstituted isomer formed only 10% of the mixture. Evidently in the present case the tendency for the pyrrolidine to conjugate with the carbon–carbon double bond [4] is strongly enhanced by the electron-withdrawing properties of the adjacent sulphonyl group,[5] thus counterbalancing the unfavourable steric interactions.

As for the reactivity of compounds (2) and (3) towards electrophiles, the former reacts only with dimethyl azodicarboxylate (DMAD), and in poor yield, to give the adduct (4) (Scheme 1). On the other hand, the analogous compound (5) is obtained quantitatively from the enamine (3), by attack of the electrophile on C-4 of the tautomeric form (3′). The adducts (4) and (5) show a C=C absorption at 1 605 and 1 595 cm^{-1}, respectively, and the signal for the proton geminal to the hydrazino group at δ 4.90 and 4.85, thus establishing their identities as substituted enaminosulphones. The latter compounds when hydrolysed both gave the ketone (6), which was identified on the basis of its elemental analysis and spectroscopic data.

The course of the reaction of the enamine (3) with diethyl azodicarboxylate (DAD) is quite similar, leading to the ketone (7) after hydrolysis of the crude reaction mixture.

For a comparison with the corresponding carbonyl analogue we could say that 2-methyl-3-pyrrolidin-1-ylcyclohex-2-en-1-one [6,7] reacts with DMAD under mild conditions, whereas with DAD it reacts only on heating under acidic catalysis, and in poor yield (see Experimental section).

Both alkylation and acylation reactions have been successful only with the enamine (3) and in yields varying from 10 to 45%. Methyl iodide reacts only in refluxing acetonitrile to give the 2,4-dimethyl substituted derivative (8) in 20% yield, after hydrolysis of the crude reaction mixture (Scheme 2). Protic solvents such as methanol do not improve the yield. Compound (8) is a product of thermodynamic control because of the reaction conditions used. This is the first example of production of a 2,4-dialkylated 5,6-dihydro-2*H*-thiopyran-3(4*H*)-one 1,1-dioxide system as far as we know.



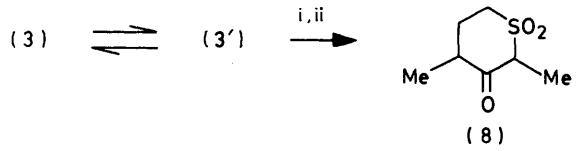
Scheme 1. *Reagents:* i, $MeO_2C{-}N{=}N{-}CO_2Me$; ii, H_3O^+

Table. Spectral data for compounds (2) and (3)

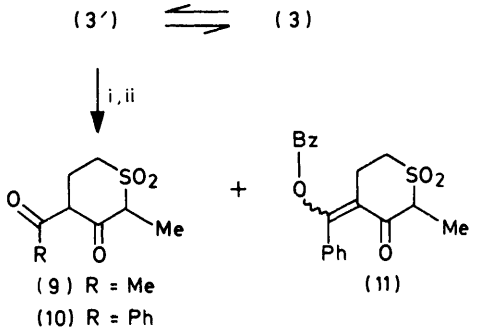
Compd.	ν(N–C=C) (cm^{-1})	$\lambda_{max.}$ (nm) (log $\varepsilon_{max.}$) *	δ(C=CH)	δ(Me)
(2)	1 650	225 (3.7)	4.9	1.55 (d)
(3)	1 580	263 (4.1)		1.95 (s)

* In EtOH.

As far as acylation is concerned, acetyl and benzoyl chlorides afford the corresponding ketones (9) and (10) after hydrolysis of the respective reaction mixtures (Scheme 3). Unfortunately large amounts of the *N*-acylated pyrrolidine are formed in both cases. In the reaction with benzoyl chloride a small amount of the enol ester (11) can also be isolated. Unlike the analogous non-methylated compound, whose enol form predominates in the equilibrium (90%),[1] only 10% of the enolic form of the ketone (9) occurs. The benzoylated system (10) shows no enolic form, like the non-methylated analogue.[1]



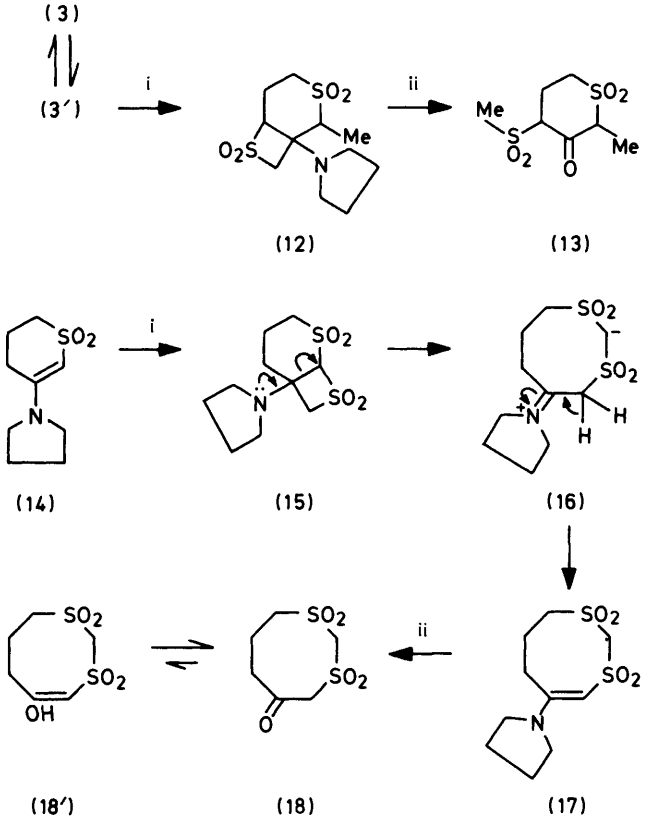
Scheme 2. *Reagents:* i, MeI, MeCN, heat; ii, H_2O



Scheme 3. *Reagents:* i, RCOCl, 80 °C; R = Me, Ph; ii, H_3O^+

Reaction of the vinylogous sulphonamide (3) with methanesulphonyl chloride furnishes the thietane 1,1-dioxide derivative (12), identified, *inter alia*, by the characteristic ABX pattern of the 6- and 8-H signals [8–10] (Scheme 4). Unlike other analogous systems derived from carbocyclic enamines,[11] compound (12) easily undergoes ring fission and subsequent hydrolysis to the ketone (13) when treated with aqueous hydrochloric acid. The instability of (12) could be ascribed to the presence of the sulphonyl group in the six-membered ring, as can be deduced from the fact that the analogous compound (15), derived from the non-methylated enaminosulphone (14), is so unstable that it cannot be isolated. Formation of compound (17) in fact follows from breaking of the bond common to the rings [12] to give the dipolar intermediate (16), whose carbanion is strongly stabilized by two adjacent sulphonyl groups. The proton transfer would lead to the vinylogous sulphonamide (17), whose n.m.r. spectrum shows a singlet at δ 5.0 for the methylene between the sulphonyl groups and a singlet at δ 4.75 for the vinyl proton. This structure is confirmed by acidic hydrolysis of the enaminosulphone (17) to give the corresponding ketosulphone (18), which exists in the enolic form (18′) to the extent of 25%, as indicated by peaks at δ 12.0 for the enol proton and δ 5.3 for the vinyl proton, both of area 0.25 H.

It is worth noting that 1-thiacyclo-octan-3-one 1,1-dioxide shows no enolic form, at least on n.m.r. analysis.[13]



Scheme 4. *Reagents:* i, $MeSO_2Cl$, NEt_3; ii, H_3O^+

Experimental

^1H N.m.r. spectra were recorded with a Bruker WP-80 spectrometer ($SiMe_4$ as internal standard, solutions in $CDCl_3$ unless otherwise stated), i.r. spectra (Nujol mulls) with a Perkin–Elmer 297 spectrophotometer, and u.v. spectra (solutions in EtOH) with a Perkin-Elmer 124 spectrophotometer. For analytical t.l.c., plates were coated with silica gel G (Merck), and for chromatographic columns extra-pure silica (Merck 70-230 mesh ASTM) was used as stationary phase.

Preparation of 2-Methyl-3-morpholin-4-yl-5,6-dihydro-2H-thiopyran 1,1-Dioxide (2).—The enamine (2) was prepared by the method of White and Weingarten [14] from the ketone (1) [1] and morpholine in benzene. After elimination of the solvent, the crude *product* was crystallized from ethanol (14% yield), m.p. 128—130 °C (Found: C, 51.6; H, 7.3; N, 5.9. $C_{10}H_{17}NO_3S$ requires C, 51.9; H, 7.4; N, 6.1%); $\nu_{max.}$ 3 080 (=CH), 1 650 (C=C), and 1 310 and 1 190 cm^{-1} (SO_2); δ 4.90 (1 H, t, vinyl-H), 4.0—3.4 (5 H, m, C*H*Me and CH_2OCH_2), 3.3—2.4 (8 H, CH_2NCH_2 and $CH_2CH_2SO_2$), and 1.55 (3 H, d, Me); $\lambda_{max.}$ (EtOH) 225 nm ($\varepsilon_{max.}$ 4 772).

Reaction of 2-Methyl-3-morpholin-4-yl-5,6-dihydro-2H-thiopyran 1,1-Dioxide (2) *with Dimethyl Azodicarboxylate.*—Dimethyl azodicarboxylate (0.13 g, 0.9 mmol) was added to a solution of the enamine (2) (0.20 g, 0.9 mmol) in dry benzene and the mixture was set aside at room temperature for 96 h. After elimination of the solvent, the residue was fractionally crystallized from absolute ethanol–light petroleum. Compound (4) (0.15 g, 45%) was separated from the ketone (1) and identified as 4-(N,N′-*dimethoxycarbonylhydrazino*)-2-*methyl*-3-*morpholin*-4-*yl*-5,6-*dihydro*-2H-*thiopyran* 1,1-*dioxide* (4), m.p. 209—211 °C (Found: C, 44.2; H, 6.0; N, 11.0. $C_{14}H_{23}N_3O_7S$ requires C, 44.6; H, 6.1; N, 11.1%); $\nu_{max.}$ 3 240 (NH), 1 758, 1 690 (CO), 1 605 (C=C), 1 525 (NH), and 1 300, 1 260, and 1 105 cm^{-1} (SO_2); δ 6.2 (1 H, bs, NH), 4.9 (1 H, bm, CH–N), 3.9—3.4 (10 H, 2s + m, 2 OMe and CH_2OCH_2), 3.4—2.2 (8 H, m, CH_2NCH_2 and $CH_2CH_2SO_2$), and 2.0 (3 H, d, *J* 1.5 Hz, Me).

Preparation of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3).—The enamine (3) was prepared by Stork condensation [4] of the ketone (1) and pyrrolidine in xylene under reflux for 24 h. After elimination of the solvent, the crude mixture was fractionally crystallized from ethanol to give the *enamine* (3) (40%), m.p. 110—112 °C (Found: C, 55.6; H, 7.8; N, 6.4. $C_{10}H_{17}NO_2S$ requires C, 55.8; H, 8.0; N, 6.5%); $\nu_{max.}$ 1 580 (C=C), and 1 330, 1 140, and 1 100 cm^{-1}

(SO_2); δ 3.25 (4 H, m, CH_2NCH_2), 2.9 (4 H, m, $CH_2CH_2SO_2$), 2.6—1.6 (9 H, m + s, $CH_2CH_2CH_2SO_2$, $CH_2CH_2CH_2N$ and Me), and 1.95 (s, Me); $\lambda_{max.}$ (EtOH) 263 nm ($\varepsilon_{max.}$ 14 155).

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Dimethyl Azodicarboxylate.*—Dimethyl azodicarboxylate (0.34 g, 2.4 mmol) was added to a solution of the enamine (3) (0.50 g, 2.32 mmol) in dry benzene and the mixture was set aside at room temperature for 72 h. The white crystalline product was filtered off (0.80 g, 96%) and crystallized from ethanol. It was identified as 4-(N,N'-*dimethoxycarbonylhydrazino*)-2-*methyl*-3-*pyrrolidin*-1-*yl*-5,6-*dihydro*-4H-*thiopyran* 1,1-*dioxide* (5), m.p. 178—179 °C (Found: C, 46.4; H, 6.3; N, 11.4. $C_{14}H_{23}N_3O_6S$ requires C, 46.5; H, 6.4; N, 11.6%); $\nu_{max.}$ 3 240 (NH), 1 760, 1 690 (CO), 1 595 (C=C), 1 530 (NH), and 1 300—1 200 and 1 100 cm^{-1} (SO_2); δ 6.4 (1 H, bs, NH), 4.85 (1 H, bm, CHN), 3.70, 3.65 (6 H, 2s, 2 OMe), 3.6—2.8 (6 H, m, CH_2NCH_2 and CH_2SO_2), 2.45 (2 H, m, $CH_2CH_2SO_2$), 2.1—1.5 (7 H, m + bs, $CH_2CH_2CH_2N$ and Me), and 1.95 (bs, Me).

Hydrolyses of Compounds (4) *and* (5).—The enamines (4) and (5) (0.2 g) were separately dissolved in ethanol and 10% hydrochloric acid was added. After 24 h at room temperature a solid was filtered off and identified as 4-(N,N'-*dimethoxycarbonylhydrazino*)-2-*methyl*-5,6-*dihydro*-2H-*thiopyran*-3(4H)-*one* 1,1-*dioxide* (6), m.p. 175—176 °C, from ethanol (Found: C, 38.8; H, 5.1; N, 8.9. $C_{10}H_{16}N_2O_7S$ requires C, 39.0; H, 5.2; N, 9.1%); $\nu_{max.}$ 3 325 (NH), 1 740, 1 715 (CO), 1 515 (NH), and 1 310, 1 150, and 1 130 cm^{-1} (SO_2); δ 6.8 (1 H, bs, NH), 5.2 (1 H, m, CHN), 4.2 (1 H, q, CHMe), 3.82, 3.80 (6 H, 2s, 2 OMe), 3.7—3.3 (2 H, m, CH_2SO_2), 2.8—1.9 (2 H, m, $CH_2CH_2SO_2$), and 1.55 (3 H, d, Me).

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Diethyl Azodicarboxylate.*—Diethyl azodicarboxylate (0.35 g, 2 mmol) was added to a solution of the enamine (3) (0.43 g, 2 mmol) in dry benzene. After 72 h at room temperature the solution was evaporated without heating, and the oily residue was hydrolysed in ethanol with 10% hydrochloric acid at room temperature for 24 h. The solution was concentrated under reduced pressure and the solid precipitated was filtered off. *Compound* (7) (0.42 g, 64%) had m.p. 131—132 °C (from ethanol) (Found: C, 42.7; H, 6.1; N, 8.2. $C_{12}H_{20}N_2O_7S$ requires C, 42.9; H, 6.0; N, 8.3%). $\nu_{max.}$ 3 330 (NH), 1 730, 1 690 (CO), and 1 310 and 1 140 cm^{-1} (SO_2); δ 6.9 (1 H, bs, NH), 5.25 (1 H, dd, CHN), 4.3 (4 H, dq, 2 $MeCH_2O$), 3.8, 3.6 (3 H, q + m, CHMe and CH_2SO_2), 2.8—2.0 (2 H, bm, $CH_2CH_2SO_2$), 1.55 (3 H, d, *J* 6.75 Hz, Me), and 1.3 (6 H, t, 2 $MeCH_2O$).

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Methyl Iodide.*—The enamine (3) (0.50 g, 2.32 mmol) in dry acetonitrile was refluxed for 12 h with a slight excess of methyl iodide. Removal of the solvent left an oil which was hydrolysed in water at room temperature and extracted with chloroform. The reaction product was isolated from the ketone (1) by column chromatography (eluant: acetone–benzene 15%) and identified as 2,4-*dimethyl*-5,6-*dihydro*-2H-*thiopyran*-3(4H)-*one* 1,1-*dioxide* (8) (0.10 g, 20%), m.p. 116—118 °C (Found: C, 47.4; H, 7.0. $C_7H_{12}O_3S$ requires C, 47.73; H, 6.87%); $\nu_{max.}$ ($CHCl_3$) 1 725 (CO), and 1 315 and 1 145 cm^{-1} (SO_2); δ 4.0 (1 H, q, CHMe), 3.4 (2 H, m, CH_2SO_2), 2.8—1.6 (3 H, m, CH_2CHMe), 1.5 (3 H, d, SO_2CHMe), and 1.2 (3 H, d, Me).

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Acetyl Chloride.*—Acetyl chloride (0.16 g, 2.0 mmol) was added to a solution of compound (3) (0.86 g, 4.0 mmol) in dry benzene and the mixture was refluxed for 3 h. The hydrochloride salt was filtered off and the solvent removed from the filtrate to leave an oily residue. This was hydrolysed in ethanol with 10% hydrochloric acid at room temperature for 24 h and the mixture extracted with chloroform. The reaction product was isolated from the ketone (1) by column chromatography (eluant: acetone–benzene, 1 : 4) and identified as 4-*acetyl*-2-*methyl*-5,6-*dihydro*-2H-*thiopyran*-3(4H)-*one* 1,1-*dioxide* (9) (0.20 g, 48%), m.p. 85—87 °C (Found: C, 47.0; H, 6.9. $C_8H_{12}O_4S$ requires C, 46.60; H, 6.8%); $\nu_{max.}$ 1 720, 1 710 (CO), and 1 315, 1 300—1 280, 1 130, and 1 110 cm^{-1} (SO_2); δ 16.5 (0.1 H, s, OH), 4.3, 4.1 (1 H, 2q, CHMe), 3.7—3.3 (3 H, m, CHCO and CH_2SO_2), 3.2—1.9 (5 H, m + s, $CH_2CH_2SO_2$ and MeCO), 2.3 (s, MeCO), and 1.5 (3 H, d, Me). With neutral ferric chloride, compound (9) gave an immediate red colouration.

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Benzoyl Chloride.*—Benzoyl chloride (0.32 g, 2.3 mmol) was added to a solution of the enamine (3) (1.0 g, 4.6 mmol) in dry benzene and the mixture was refluxed for 24 h. The hydrochloric salt was filtered off and the mother liquors concentrated. The residue was hydrolysed and extracted with chloroform to furnish a mixture of compounds (1), (10), and (11), and the pyrrolidinylbenzamide which had been separated by column chromatography. Compound (10) (0.28 g, 45%) was identified as 4-*benzoyl*-2-*methyl*-5,6-*dihydro*-2H-*thiopyran*-3(4H)-*one* 1,1-*dioxide*, m.p. 190—191 °C (from ethanol) (Found: C, 58.7; H, 5.5. $C_{13}H_{14}O_4S$ requires C, 58.6; H, 5.3%); $\nu_{max.}$ 1 718, 1 680 (CO), 1 595, 1 580, 1 400, 765, 710 (Ph), 1 320, 1 290, 1 140, and 1 115 cm^{-1} (SO_2); δ (CD_3CN) 8.0 (2 H, m, *o*-ArH), 7.6 (3 H, m, *m*- and *p*-ArH), 4.9 (1 H, dd, CHCOPh), 4.6 (1 H, q, CHMe), 3.6 (2 H, m, CH_2SO_2), 2.5 (2 H, m, $CH_2CH_2SO_2$), and 1.4 (3 H, d, Me). With neutral ferric chloride, compound (10) gave an immediate red colouration.

4-*Benzoyloxy*(*phenyl*)*methylene*-2-*methyl*-2H-*thiopyran*-3(4H)-*one* (11) (0.04 g, 5%) had m.p. 140—141 °C from ethanol (Found: C, 65.0; H, 5.0. $C_{20}H_{18}O_5S$ requires C, 64.9; H, 4.9%); $\nu_{max.}$ 1 730, 1 705 (CO), 1 645 (C=C), 1 595, 760, 710 (Ph), 1 315, 1 290, and 1 130 cm^{-1} (SO_2); δ(CD_3CN) 8.2 (2 H, m, *o*-ArH), 7.5 (8 H, m, *m*- and *p*-ArH), 4.6 (1 H, q, CHMe), 3.5 (2 H, m, CH_2SO_2), 3.0 (2 H, m, $CH_2CH_2SO_2$), and 1.5 (3 H, d, Me).

The remainder was identified as pyrrolidinylbenzamide (0.08 g, 21%).

Reaction of 2-Methyl-3-pyrrolidin-1-yl-5,6-dihydro-4H-thiopyran 1,1-Dioxide (3) *with Methanesulphonyl Chloride.*—Methanesulphonyl chloride (0.23 g, 2.0 mmol) was added dropwise to a solution of the enamine (3) (0.43 g, 2.0 mmol) and triethylamine (0.20 g, 2.0 mmol) in dry benzene. The mixture was stirred at room temperature for 24 h. The hydrochloride salt was filtered off and the solvent removed. The oily residue was chromatographed on a column (eluant: acetone–benzene, 1 : 4). The separation furnished compound (1), pyrrolidinesulphonamide (0.06 g, 17%), and compound (12) (0.12 g, 20%) which was identified as 2-*methyl*-1-*pyrrolidin*-1-*yl*-3,7-*dithiabicyclo*[4.2.0]*octane* 3,3,7,7-*tetraoxide*, m.p. 130—131 °C (from ethanol) (Found: C, 45.0; H, 6.3; N, 4.7. $C_{11}H_{19}NO_4S_2$ requires C, 45.5; H, 6.5; N, 4.8%); $\nu_{max.}$ 1 320—1 290 and 1 140—1 110 cm^{-1} (SO_2); δ 4.8, 4.2 (2 H, 2 dd, 2 8-H), 4.5 (1 H, m, 6-H), 4.0—2.1 (9 H, m, CHMe, $CH_2CH_2SO_2$, and CH_2NCH_2), 1.8 (4 H, m, $CH_2CH_2CH_2N$), and 1.35 (3 H, d, Me). Compound (12) was easily hydrolysed in ethanol–water under reflux to give (13), identified as 2-*methyl*-4-*methylsulphonyl*-5,6-*dihydro*-2H-*thio*-

pyran-3(4H)-*one* 1,1-*dioxide*, m.p. 198—199 °C (from benzene) (Found: C, 34.9; H, 5.7. $C_7H_{12}O_5S_2$ requires C, 35.0; H, 5.8%); $\nu_{max.}$ 1 725 (CO), and 1 305, 1 140, and 1 110 cm^{-1} (SO_2); δ[$(CD_3)_2SO$] 4.7 (2 H, m, C*H*Me and C*H*SO_2Me), 3.75 (2 H, m, CH_2SO_2), and 3.1 (3 H, s, Me).

Reaction of 3-*Pyrrolidin*-1-*yl*-5,6-*dihydro*-4H-*thiopyran* 1,1-*Dioxide* (14) *with Methanesulphonyl Chloride*.—Methanesulphonyl chloride (1.14 g, 10 mmol) was added dropwise to a solution of the enamine (14) (2.0 g, 10 mmol) and triethylamine (1.0 g, 10 mmol) in dry benzene. The mixture was stirred at room temperature for ½ h and the hydrochloride salt filtered off. The mother-liquors were concentrated to furnish compound (17) (2.5 g, 90%), identified as 5-*pyrrolidin*-1-*yl*-1,3-*dithiacyclo-oct*-4-*ene* 1,1,3,3-*tetraoxide*, m.p. 185 °C (from ethanol) (Found: C, 42.8; H, 6.2; N, 4.8. $C_{10}H_{17}NO_4S_2$ requires C, 43.0; H, 6.1; N, 5.0%); $\nu_{max.}$ 1 545 (C=C), and 1 315, 1 290, 1 280, and 1 125 cm^{-1} (SO_2); δ[$(CD_3)_2SO$] 5.0 (2 H, s, $SO_2CH_2SO_2$), 4.75 (1 H, s, vinyl-H), 3.90—2.65 (8 H, m, $CH_2CH_2SO_2$ and CH_2NCH_2), and 2.40—1.45 (6 H, m, $CH_2CH_2CH_2SO_2$ and $CH_2CH_2CH_2N$).

Hydrolysis of Compound (17).—The enamine (17) in acetonitrile was treated with 10% hydrochloric acid, with stirring, at room temperature for 12 h. Removal of the solvent furnished 1,3-*dithiacyclo-octan*-5-*one* 1,1,3,3-*tetraoxide* (18), m.p. 200 °C (from ethyl acetate) (Found: C, 31.6; H, 4.3. $C_6H_{10}O_5S_2$ requires C, 31.9; H, 4.5%); $\nu_{max.}$ 1 710 (CO), and 1 335—1 300 and 1 135 cm^{-1} (SO_2); δ[$(CD_3)_2SO$] 12.0 (0.25 H, s, OH), 5.75 (2 H, s, $SO_2CH_2SO_2$), 5.3 (0.25 H, s, vinyl-H), 4.7 (1.75 H, s, $COCH_2SO_2$), 3.5 (2 H, m, CH_2SO_2), 2.9 (2 H, m, CH_2CO), and 2.3 (2 H, m, CH_2CH_2CO).

Reaction of 2-*Methyl*-3-*pyrrolidin*-1-*ylcyclohex*-2-*en*-1-*one with Dimethyl Azodicarboxylate*.—Dimethyl azodicarboxylate (0.76 g, 5.2 mmol) was added to a solution of the enaminone (1.0 g, 5.2 mmol) in dry diethyl ether and the mixture was set aside at room temperature for 12 h. The precipitate was filtered off (1.4 g, 78%), and identified as 4-(N,N′-*dimethoxycarbonylhydrazino*)-2-*methyl*-3-*pyrrolidin*-1-*ylcyclohex*-2-*en*-1-*one*, m.p. 202—203 °C (Found: C, 56.0; H, 6.8; N, 13.1. $C_{15}H_{23}N_3O_5$ requires C, 55.4; H, 7.1; N, 12.9%); $\nu_{max.}$ ($CHCl_3$) 3 370 (NH), 1 750, 1 705 (CO), and 1 540 cm^{-1} (C=C); δ 7.4 (1 H, bs, NH), 5.3 (1 H, bm, CHN), 4.0—3.1 (10 H, m + 2s, CH_2NCH_2 and 2 OMe), 3.9 and 3.75 (2s, OMe), 2.9—1.6 (11 H, m + s, CH_2CH_2CO, $CH_2CH_2CH_2N$ and Me), and 2.0 (s, Me).

Reaction of 2-*Methyl*-3-*pyrrolidin*-1-*ylcyclohex*-2-*en*-1-*one with Diethyl Azodicarboxylate*.—Diethyl azodicarboxylate (1.4 g, 7.8 mmol) was added to a solution of the enaminone (1.5 g, 7.8 mmol) in dry benzene containing toluene-*p*-sulphonic acid and the mixture was refluxed for 72 h. After elimination of the solvent and treatment with diethyl ether, the precipitate was filtered off (0.67 g, 23%), and identified as 4-(N,N′-*diethoxycarbonylhydrazino*)-2-*methyl*-3-*pyrrolidin*-1-*ylcyclohex*-2-*en*-1-*one*, m.p. 147—148 °C (Found: C, 58.1; H, 7.9; N, 11.9. $C_{17}H_{27}N_3O_5$ requires C, 57.8; H, 7.7; N, 11.9%); $\nu_{max.}$ ($CHCl_3$) 3 370 (NH), 1 750, 1 700 (CO), and 1 550 (C=C); δ 7.1—6.5 (1 H, 2bs, NH), 5.25 (1 H, bm, CHN), 4.5—3.1 (8 H, m + 2q, CH_2NCH_2 and 2 CH_2Me), 2.7—1.7 (11 H, m + s, $CH_2CH_2CH_2N$, CH_2CH_2CO, and Me), 1.95 (s, Me), and 1.3 (6 H, 2 t, CH_2Me).

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