Synthesis of Dipyrazolo[3,4-*b*:4′,3′-*f*]azepines and Dithieno[2,3-*b*:3′,2′*f*]-azepines from 1-Substituted 2,7-Dichloro-4,5-dihydro-1*H*-azepine-3,6-dicarbaldehydes

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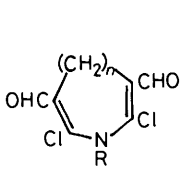
Syntheses of the title compounds (**7**) and (**8**) are described. These new bis-heterocyclic analogues of dibenzo[*b*,*f*]azepines (**4**) were readily obtained from the di-β-chlorovinyl aldehydes (**3**), the latter prepared by formylation of the azepines (**5**). The thiophene analogue (**10**) of the antidepressant 'imipramine' was then synthesized by debenzylation of the dithienoazepine (**8a**) followed by condensation with an appropriate halide.

Various heterocyclic compounds are readily available from β-chlorovinyl aldehydes.[1] Accordingly, di-β-chlorovinyl aldehydes (**1**)—(**3**) appear to be useful starting materials for the synthesis of a wide range of tricyclic systems. The preparation of (**1**)[2] and (**2**)[3] has been reported but the azepine derivatives (**3**) are so far unknown, making access to the bis-heterocyclic isosteres of dibenzo[*b*,*f*]azepines (**4**)[4] difficult. Indeed, while some monothiophene[5,6] and monopyrimidine[7,8] analogues of (**4**) have been described, only one pyridine bis-heterocyclic analogue of (**4**) has been synthesized.[9]

In the course of our studies directed towards the synthetic utility of azides[10] and iminophosphoranes[11], we have previously shown[12] that the azepines (**5**) are available from organic azides by addition of triphenylphosphine at room temperature and *in situ* condensation of the resulting iminophosphoranes with adipoyl chloride in refluxing toluene or benzene. We report here the preparation of the new di-β-chlorovinyl aldehydes (**3**) from the azepines (**5**) as well as the first synthesis of bisthiophene and bispyrazole isosteres of dibenzo[*b*,*f*]azepines (**4**).

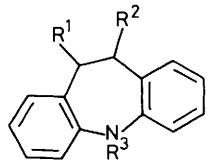
Treatment of the azepine (**5a**) with the Vilsmeier reagent,[13] diluted in dichloromethane in the customary proportions[14] (4 equiv. of Vilsmeier reagent), led to isolation of a mixture of the azepines (**6**) and (**3a**) in 35 and 10% yields, respectively. The azepine (**6**) is very unstable, like a number of mono-β-chlorovinyl aldehydes,[15] and consequently could not be used as an intermediate to prepare the target (**3**). The azepines (**5**) were submitted to greater excesses of Vilsmeier reagent and longer refluxing times until the reaction produced solely the desired di-β-chlorovinyl aldehydes (**3**) in 62—66% yields. The azepine (**3b**) was isolated as an oil which decomposed slowly at 0 °C; in contrast, the azepines (**3a**) and (**3c**) have high m.p.s and are very stable compounds, making them attractive as starting materials.

A number of monopyrazole isosteres of dibenzo[*c*,*e*]azepines have been described,[16,17] and showed interesting biological properties,[18,19] but there appear to be no syntheses to date of mono- or bis-pyrazole analogues of dibenzo[*b*,*f*]azepine (**4**). On condensation with phenylhydrazine in acetic acid,[20] the di-β-chlorovinyl aldehydes (**3a**) and (**3c**) gave high yields of dipyrazolo[*b*,*f*]azepines (**7**) [compound (**3b**) was not used in this reaction because the ester group was likely to react with the solvent]. The analytical and spectroscopic data for the dipyrazolo[*b*,*f*]azepines (**7**) were in good agreement with the proposed structure. The mass spectra of compounds (**7**) showed the great stability of their structure since the cleavages of the *N*-substituent bonds were the only significant fragmentations. In

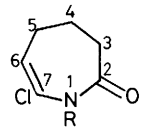


(**1**) *n* = 0
(**2**) *n* = 1
(**3**) *n* = 2

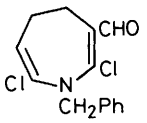
a; R = CH_2Ph
b; R = CH_2CO_2Et
c; R = Ph



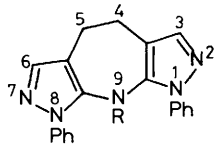
(**4**)



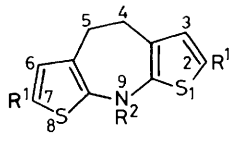
(**5a**) R = CH_2Ph
(**5b**) R = CH_2CO_2Et
(**5c**) R = Ph



(**6**)



(**7a**) R = CH_2Ph
(**7b**) R = Ph



(**8a**) R^1 = CO_2Et, R^2 = CH_2Ph
(**8b**) R^1 = CO_2Et, R^2 = CH_2CO_2Et
(**8c**) R^1 = CO_2Et, R^2 = Ph
(**9**) R^1 = CO_2Et, R^2 = H
(**10**) R^1 = CO_2Et, R^2 = $(CH_2)_3NMe_2$
(**11**) R^1 = CO_2H, R^2 = CH_2Ph
(**12**) R^1 = H, R^2 = CH_2Ph
(**13**) R^1 = R^2 = H

the ^1H n.m.r. spectra, the symmetrical nature of (**7**) was proved by the equivalence of the two pyrazole protons. Furthermore, in the spectrum of (**7a**) all of the aromatic multiplets could be unambiguously attributed owing to the absence of overlapping, and the *ortho*, *meta*, and *para* protons of the two benzene rings bonded to the pyrazole nitrogens were equivalent. In addition,

Table 1. ^{1}H N.m.r. spectra of dithieno[*b*,*f*]azepines

Compd.	4-H_2, 5-H_2	3-H, 6-H	Chemical shifts (p.p.m.) R^1	Chemical shifts (p.p.m.) R^2	Coupling constants *J*/Hz
(8a)[a]	2.97 (s, 4 H)	7.36 (s, 2 H)	CH_2CH_3:4.26 (q, 4 H) CH_2CH_3:1.31 (t, 6 H)	NCH_2:5.15 (s, 2 H) ArH:7.28—7.33 (m, 5 H)	J_{CH_2,CH_3} 7.08
(8b)[a]	2.97 (s, 4 H)	7.37 (s, 2 H)	CH_2CH_3:4.29 (q, 4 H) CH_2CH_3:1.33 (t, 6 H)	NCH_2:4.58 (s, 2 H) CH_2CH_3:4.30 (q, 2 H) CH_2CH_3:1.32 (t, 3 H)	$J_{CH_2,CH_3(R)} = J_{CH_2,CH_3(R')} = 7.12$
(8c)[a]	3.04 (s, 4 H)	7.39 (s, 2 H)	CH_2CH_3:4.22 (q, 4 H) CH_2CH_3:1.27 (t, 6 H)	ArH:7.46—7.62 (m, 5 H)	J_{CH_2,CH_3} 7.14
(9)[b]	2.92 (s, 4 H)	7.42 (s, 2 H)	CH_2CH_3:4.24 (q, 4 H) CH_2CH_3:1.29 (t, 6 H)	NH:10.86 (br s, 1 H) (exchange with D_2O)	J_{CH_2,CH_3} 7.00
(10)[a]	2.92 (s, 4 H)	7.36 (s, 2 H)	CH_2CH_3:4.30 (q, 4 H) CH_2CH_3:1.35 (t, 6 H)	1′-H_2 or 3′-H_2:3.96 (t, 2 H) 2′-H_2:2.06 (quint, 2 H) 1′-H_2 or 3′-H_2:2.37 (t, 2 H) NMe_2:2.23 (s, 6 H)	J_{CH_2,CH_3} 7.09 $J_{1'-H_2,2'-H_2}$ } 7.6 and 6.9 $J_{2'-H_2,3'-H_2}$ }
(12)[b]	2.89 (s, 4 H)	6.69 (d, 2 H)	2-H and 7-H:6.83 (d, 2 H)	NCH_2:4.97 (s, 2 H) ArH:7.28—7.39 (m, 5 H)	$J_{2-H,3-H}$ 5.55
(13)[b]	2.86 (s, 4 H)	6.55 (d, 2 H)	2-H and 7-H:6.59 (d, 2 H)	NH:9.45 (br s, 1 H) (exchange with D_2O)	$J_{2-H,3-H}$ 5.44

[a] In $CDCl_3$. [b] In $(CD_3)_2SO$.

the two methylene groups of the azepine ring gave two multiplets for (**7a**) and one singlet for (**7b**), thus showing the greater flexibility of the latter.

We next investigated the synthesis of bisthiophene isosteres of dibenzo[*b*,*f*]azepines (**4**). These analogues seemed to us to be of special interest because the replacement of one or both of the flanking benzene rings of the related dibenzo[*b*,*e*]azepines[21,22] or dibenzo[*a*,*d*]cycloheptenes[23] by a thiophene ring has been achieved and led to compounds with useful biological activities. In contrast, only monothiophene isosteres of dibenzo[*b*,*f*]azepines have hitherto been synthesized.[4-6] The latter showed a pharmacological profile similar to that of the benzene parent and in some cases[6] a lesser degree of cardiac toxicity. Thus, di-β-chlorovinyl aldehydes (**3**) were converted in one step into the dithieno[*b*,*f*]azepines (**8**) in good yields by condensation with ethyl 2-mercaptoacetate and triethylamine in pyridine.[24] An important structural requirement[4] for activity of dibenzo[*b*,*f*]azepines and related compounds is the presence of a three-carbon aliphatic chain with a terminal amino group on the azepine nitrogen as illustrated by the antidepressant imipramine [**4**; $R^1 = R^2 = H$, $R^3 = (CH_2)_3NMe_2$]. We therefore decided to show the usefulness of our method for biological purposes by preparing a dithienoazepine with such a side-chain. Thus, debenzylation of (**8a**) was attempted by classical methods, but only a modification of a recent one[25] involving treatment with aluminium chloride in benzene was successful. Reaction with sodium hydride in benzene followed by condensation with a suitable halide using Villani's procedure[9] then led to the desired dithienoazepine (**10**). An attempt was also made to prepare the analogue of (**10**) having unsubstituted thiophene rings. To this end, the di-β-chlorovinyl aldehyde (**3a**) was treated with 2-mercaptoacetic acid and triethylamine in pyridine.[26] Refluxing of the mixture for 12 h effected decarboxylation of the intermediate diacid (**11**) and the dithienoazepine (**12**) was directly obtained in 60% yield. Debenzylation of (**12**) was also achieved by treatment with aluminium choride in benzene. However, only a very low yield of the dithieno[*b*,*f*]azepine (**13**) could be obtained, owing to the expected great instability of this derivative. Indeed, the two thiophene rings of (**13**) are substituted by an amino group in the α-position, and α-amino thiophene derivatives are stable only if they are also substituted by an electron-withdrawing group.[27]

From the mass spectra of compounds (**8**)—(**10**) and (**12**), it can be seen that the stability of the dithieno[*b*,*f*]azepine skeleton is comparable to that of the pyrazole derivatives: the molecular ions are the base peaks except in the cases of the *N*-benzyldithienoazepines (**8a**) [base peak: $(M - C_6H_5CH_2)^+$] and (**12**) [base peak: $(C_6H_5CH_2)^+$] and of compound (**10**). In the latter case, the base peak results from the expected facile fragmentation of the aliphatic chain at the position β to the amino group.[28] In the ^{1}H n.m.r. spectra of all the dithienoazepines (**8**)—(**10**), (**12**), and (**13**) (Table 1), the thiophene protons and the protons of the ethyl carboxylate groups of the thiophene rings each appear as single signals. In addition, the rapid exchange between the possible conformations of the azepine ring was evidenced by the presence of only one singlet for the azepine methylene groups.

Experimental

M.p.s were determined on a Kofler heated stage, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 B spectrophotometer. ^{1}H N.m.r. spectra were obtained on a Bruker WM 400 (400 MHz) spectrometer of the CEREMA ('Centre de Résonance Magnétique' of the University of Bourgogne). ^{1}H N.m.r. of (**3a**—**c**) and (**6**) are reported in Table 2. Mass spectra were recorded on a Finnigan 3300 mass spectrometer, using electron-impact ionization (70 eV).

1-Benzyl-2,7-Dichloro-4,5-dihydro-1H-azepine-3-carbaldehyde (**6**) *and 1-Benzyl-2,7-Dichloro-4,5-dihydro-1H-azepine-3,6-dicarbaldehyde* (**3a**).—To dimethylformamide (3.7 ml, 48 mmol) was added dropwise at 0 °C freshly distilled phosphorus oxychloride (4.5 ml, 48 mmol) immediately followed by anhydrous dichloromethane (15 ml); the solution was then heated at 100 °C for 2 h. The reaction mixture was allowed to cool to room temperature and a solution of the azepine (**5a**) (2.83 g, 12 mmol) in dichloromethane (35 ml) was added dropwise. After refluxing for 12 h, the solution was added dropwise to 40% aqueous sodium acetate (70 ml) at such a rate as to maintain the temperature below 10 °C with ice-bath cooling. After the mixture had been stirred at room temperature for 2 h, the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with 5% aqueous sodium carbonate and water, dried, and evaporated under reduced pressure. Chromatography of the residue over alumina

Table 2. ^1H N.m.r. spectra of mono- and di-β-chlorovinyl aldehydes (**3**) and (**6**) in $CDCl_3$.

Compd.	Chemical shifts (p.p.m.) 4-H_2 and 5-H_2	CHO	6-H	R	Coupling constants *J*/Hz
(**3a**)	2.31 (s, 4 H)	10.01 (s, 2 H)		NCH_2:4.99 (s, 2 H) ArH:7.31—7.37 (m, 5 H)	
(**3b**)	2.69 (s, 4 H)	10.02 (s, 2 H)		NCH_2:4.61 (s, 2 H) CH_2CH_3:4.25 (q, 2 H) CH_2CH_3:1.31 (t, 3 H)	J_{CH_2,CH_3}7.15
(**3c**)	2.71 (s, 4 H)	10.05 (s, 2 H)		ArH:7.43—7.48 (m, 5 H)	
(**6**)	2.02 (m, 2 H) 2.27 (m, 2 H)	9.99 (s, 1 H)	5.55(t,1 H)	NCH_2:4.79 (s, 2 H) ArH:7.33—7.35 (m, 5 H)	J_{H_5,H_6}5.4

eluting with dichloromethane gave the azepine (**6**) (1.18 g, 35%) as an oil, which decomposed rapidly, and the azepine (**3a**) (0.37 g, 10%) as yellow *needles*, m.p. 147—148 °C (from dichloromethane) (Found: C, 58.3; H, 4.35; Cl, 22.8; N, 4.6. $C_{15}H_{13}Cl_2NO_2$ requires C, 58.08; H, 4.22; Cl, 22.86; N, 4.52%); $\nu_{max.}$(CsI) 2 932 and 2 892 (CH_2 and CHO), 1 666 (CO), 1 627 (C=C), 1 582, 1 369, 1 214, and 1 192 cm^{-1}; *m/z* 311 (0.2), 309 (M^+, 0.2%), 283 (4), 281 (5), and 91 (100).

Formylations using a Large Excess of Vilsmeier Reagent.—The above procedure was used with the following modifications: after addition of the Vilsmeier reagent (0.14 mol instead of 48 mmol) to the azepine (**5**) (12 mmol), the reaction mixture was refluxed for 3 days. The residue obtained after hydrolysis by 40% aqueous sodium acetate (260 ml) and work-up as above was not chromatographed but recrystallized to give the pure di-β-chlorovinyl aldehyde (**3**). In the case of (**3a**), a 62% yield was obtained.

Ethyl 2-(2,7-*dichloro*-3,6-*diformyl*-4,5-*dihydro*-1H-*azepine*-1-*yl*)*acetate* (**3b**). Colourless oil (65%); $\nu_{max.}$(film) 2 979 and 2 872 (CH_2 and CHO), 1 745 (COOEt), 1 678 (COH), 1 625 (C=C), 1 584, and 1 198 cm^{-1}; elemental analysis and mass spectrum could not be obtained due to the rapid decomposition of the product which was used immediately for the preparation of (**8b**).

2,7-*Dichloro*-1-*phenyl*-4,5-*dihydro*-1H-*azepine*-3,6-*dicarbaldehyde* (**3c**). Yellow needles, (66%); m.p. 111 °C (from diethyl ether–heptane) (Found: C, 56.9; H, 3.65; Cl, 24.0; N, 4.6. $C_{14}H_{11}Cl_2NO_2$ requires C, 56.78; H, 3.74; Cl, 23.94; N, 4.73%); $\nu_{max.}$(KBr) 2 885 and 2 870 (CH_2 and CHO), 1 665 (CO), 1 620 (C=C), 1 574, and 1 237 cm^{-1}; *m/z* 299 (1), 298 (2), 297 (12), 296 (5), 295 (M^+, 19%), 269 (66), 267 (100), 238 (28), 232 (48), 204 (26), 168 (44), 138 (36), 104 (29), and 77 (63).

Dipyrazolo[b,f]*azepines* (**7**).—*General procedure.* Phenylhydrazine (1.23 ml, 12.5 mmol) was poured into a solution of the di-β-chlorovinyl aldehyde (**3**) (2.5 mmol) in acetic acid (15 ml). The reaction mixture was refluxed for 1 h and then evaporated under reduced pressure. The residue was dissolved in dichloromethane and the resulting solution was washed with 5% aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated to dryness. Recrystallization of the residue from dichloromethane–hexane (4:1) gave pure title compound (**7**).

9-*Benzyl*-1,8-*diphenyl*-4,5,8,9-*tetrahydro*-1H-*dipyrazolo*[3,4-b:4′,3′-f]*azepine* (**7a**). Yellow needles, (82%); m.p. 198 °C (Found: C, 77.7; H, 5.4; N, 17.05. $C_{27}H_{23}N_5$ requires C, 77.67; H.5.55; N, 16.77%); $\nu_{max.}$(CsI) 3 052, 2 918, 1 598, 1 499, 1 482, and 1 453 cm^{-1}; δ_H($CDCl_3$) 1.96 and 2.43 (2 × 2 H, 2 × m, 4-H_2 and 5-H_2), 3.53 (2 H, s, NCH_2), 6.45 (2 H, m, 2′- and 6′- NArH), 7.17 (2 H, m, 3′ and 5′-NArH), 7.27 (1 H, m, 4′-NArH), 7.44 (2 H, s, 3-H and 6-H), 7.49 (2 H, m, 2 × 4″-NNArH), 7.58 [4 H, m, 2 × (3″- and 5″-NNArH)], and 7.72 [4 H, m, 2 × (2″- and 6″-NN-Arh)]; *m/z* 418 (17), 417 (M^+, 47%), 326 (100), 91 (18), 77 (32), and 44 (55).

1,8,9-*Triphenyl*-4,5,8,9-*tetrahydro*-1H-*dipyrazolo*[3,4-b:4′,3′-f]*azepine* (**7b**). Orange needles (83%); m.p. 194 °C (Found: C, 76.0; H, 5.25; N, 17.15. $C_{26}H_{21}N_5$ requires C, 77.40; H, 5.25; N, 17.36%); $\nu_{max.}$(CsI) 3 279, 1 641, 1 595, and 1 501 cm^{-1}; δ_H ($CDCl_3$) 2.71 (4 H, s, 4-H_2 and 5-H_2), 6.50—7.40 (15 H, m, ArH), and 7.74 (2 H, s, 3-H and 6-H); *m/z* 403 (M^+, 100%), 326 (10), and 77 (46).

Dithieno[b,f]*azepines* (**8**).—*General procedure.* To a stirred solution of the di-β-chlorovinyl aldehyde (**3**) (0.02 mol) in pyridine (80 ml, dried over potassium hydroxide) was added dropwise at room temperature ethyl 2-mercaptoacetate (4.1 ml, 0.05 mol). The solution was cooled to 0 °C and triethylamine (9.7 ml, 0.07 mol) was added very slowly. The reaction mixture was refluxed for 2.5 h, and then stirred at room temperature for 10 h. Continuation of the procedure depended on the starting material. (*a*) When (**3c**) was the starting azepine, a solid separated out on cooling; this was filtered off, washed with water, and dried under reduced pressure. Recrystallization from ethyl acetate afforded pure dithienoazepine (**8c**). (*b*) Starting from (**3a**) or (**3b**), 50% aqueous potassium hydroxide (10 ml) was added dropwise at 0 °C to the reaction mixture. Stirring was continued for 1 h at room temperature and then the solution was poured into water (250 ml) cooled to 5 °C. A yellow solid precipitated immediately, and was filtered off and dried under reduced pressure. Recrystallization from ethyl acetate gave pure dithienoazepine (**8a**) or (**8b**).

Diethyl 9-*Benzyl*-4,5-*dihydro*-9H-*dithieno*[2,3-b:3′,2′-f]*azepine*-2,7-*dicarboxylate* (**8a**). Needles (83%); m.p. 136—137 °C (Found: C, 62.6; H, 5.35; N, 3.15; S, 14.6. $C_{23}H_{23}NO_4S_2$ requires C, 62.56; H, 5.25; N, 3.17; S, 14.52%); $\nu_{max.}$(KBr) 1 685 (COOEt), 1 433, 1 283, 1 198, and 1 079 cm^{-1}; *m/z* 441 (M^+, 25%), 350 (100), and 91 (17).

Diethyl 9-*Ethoxycarbonylmethyl*-4,5-*dihydro*-9H-*dithieno*-[2,3-b:3′,2′-f]*azepine*-2,7-*dicarboxylate* (**8b**). Needles (70%); m.p. 90—92 °C (Found: C, 54.95; H, 5.3; N, 3.2; S, 14.4. $C_{20}H_{23}NO_6S_2$ requires C, 54.90; H, 5.30; N, 3.20; S, 14.66%); $\nu_{max.}$(KBr) 1 750 (CH_2CO_2Et), 1 693 (=CCO_2Et), 1 455, 1 433, 1 245, and 1 199 cm^{-1}; *m/z* 437 (M^+, 100%), 364 (24), 350 (14), and 336 (20).

Diethyl 9-*Phenyl*-4,5-*dihydro*-9H-*dithieno*[2,3-b:3′,2′-f]*azepine*-2,7-*dicarboxylate* (**8c**). Needles (68%); m.p. 190 °C (Found: C, 61.5; H, 4.85; N, 3.25; S, 15.1. $C_{22}H_{21}NO_4S_2$ requires C, 61.81; H, 4.95; N, 3.28; S, 15.00%); $\nu_{max.}$(KBr) 1 686 (COOEt), 1 432, and 1 274 cm^{-1}; *m/z* 427 (M^+, 100%), 399 (13), 382 (9), and 371 (9).

Diethyl 4,5-*Dihydro*-9H-*dithieno*[2,3-b:3′,2′-f]*azepine*-2,7-*dicarboxylate* (**9**).—A solution of the dithienoazepine (**8a**) (1.5 g, 3.4 mmol) in dry benzene (150 ml) was poured onto freshly

sublimed aluminium chloride. The reaction mixture was then refluxed for 0.5 h, washed with water, and dried ($MgSO_4$). After evaporation to dryness, the residue was recrystallized from dichloromethane–hexane (3:1) to give the title compound (**9**) (0.48 g, 40%) as green needles [which were used without further purification for the preparation of the target dithienoazepine (**10**)], m.p. 222 °C; $\nu_{max.}$ (CsI) 3 452 (NH), 1 665 (COOEt), 1 451, and 1 244 cm^{-1}; *m/z* 351 (M^+, 100%), 323 (12), 306 (14), and 295 (10).

Diethyl 9-(3-*Dimethylaminopropyl*)-4,5-*dihydro*-9H-*dithieno*-[2,3-b:3′,2′-f]*azepine*-2,7-*dicarboxylate* (**10**).—Villani's procedure[9] was used. Yield 65%, m.p. 99 °C (from diethyl ether–hexane) (Found: C, 57.1; H, 6.45; N, 6.7; S, 14.75. $C_{21}H_{28}N_2O_4S_2$ requires C, 57.77; H, 6.46; N, 6.42; S, 14.69%); $\nu_{max.}$(CsI) 1 695 (CO_2Et), 1 453, and 1 429 cm^{-1}; *m/z* 436 (M^+, 28%), 86 (54), 71 (20), and 58 (100).

9-*Benzyl*-4,5-*dihydro*-9H-*dithieno*[2,3-b:3′,2′-f]*azepine* (**12**).—To a stirred solution of (**3a**) (1.86 g, 6 mmol) in pyridine (25 ml, dried over potassium hydroxide) was added dropwise at 0 °C 2-mercaptoacetic acid (1.25 ml, 18 mmol), and triethylamine (3.7 ml, 27 mmol). The mixture was stirred for 15 min at 0 °C and then 4 h at room temperature after which it was refluxed for 12 h and then poured into 5% aqueous sodium hydroxide (20 ml). The aqueous layer was extracted with diethyl ether and the combined organic layers were washed successively with 25% aqueous hydrochloric acid, saturated aqueous $NaHCO_3$, and water, dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography of the residue over silica gel, eluting with dichloromethane–hexane (4:1), followed by recrystallization from diethyl ether–hexane (1:1) afforded pure title compound (**12**) (1.07 g, 60%) as green *needles*, m.p. 80 °C (Found: C, 68.2; H, 5.0; N, 4.7; S, 21.55. $C_{17}H_{15}NS_2$ requires C, 68.65; H, 5.08; N, 4.71; S, 21.56%); $\nu_{max.}$(CsI) 2 898 (CH_2), 1 551, 1 461, 1 448, 1 358, and 1 214 cm^{-1}; *m/z* 297 (M^+, 78%), 206 (92), 173 (57), and 91 (100).

References

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