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RESEARCH ARTICLE

Unsaturated sulfur compounds from reactions of lithiated methylazines with carbon disulfide and electrophiles

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2-Methylpyridine (**1a**), 2,6-dimethylpyridine (**1b**), 2-methylpyrazine (**1c**) and 2-methylquinoline (**1d**) were treated with lithium diisopropylamide (LDA) in THF at low temperature followed by carbon disulfide to give the dianion (**5**). Reactions of dianion (**5**) with iodomethane, 1,2-dibromoethane, ethyl chloroacetate, α-chloroacetonitrile or phenacyl bromide gave **6a–c**, **6e**, **9**, **10**, **11**, **12** and **13**, respectively. Reactions of dianion (**5**) with 1,2-dibromoethene gave the dithiocarboxylic acids (**14a–c**) rather than a dithiolene, and reaction of dianion (**5a**) with aqueous ammonium persulfate gave **15**. Treatment of 2-methylpyridine (**1a**) with lithium diisopropylamide (LDA) and 2-bromopyridine afforded tetra-2-pyridylmethane (**18**) as the main product.

Keywords: 2-Methylpyridine; 2,6-Dimethylpyridine; 2-Methylpyrazine; 2-Methylqunoxaline; LDA; Carbon disulfide; Alkylation

1. Introduction

Addition of organolithium compounds to thiocarbonyl groups to form carbon–carbon bonds is not on the whole of great practical value [1–4]. The exception is addition to cumulated thiocarbonyl groups, and particularly to carbon disulfide, which is a useful method for preparing dithiocarboxylates (**4**) and compounds that can be made from them *in situ* [5–8], as shown in scheme 1. The products of such reactions, especially the ketenedithioacetals (**6**) are in turn useful intermediates for further synthesis.

Reaction of some 2-methylazines with LDA and carbon disulfide, followed by alkylation with 1,2-dibromoethane or 1,3-dibromopropane were reported to give the corresponding methylenedithiolanes (**7**) or methylenedithianes (**8**) [9]. Other examples are based

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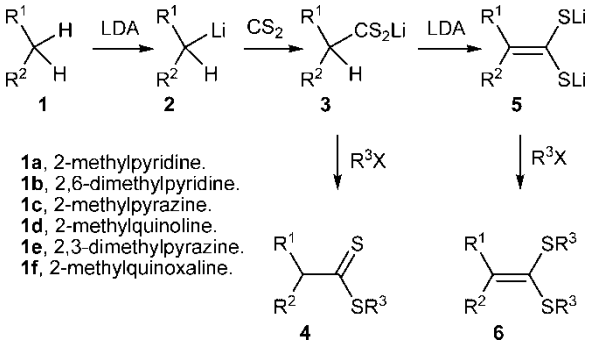
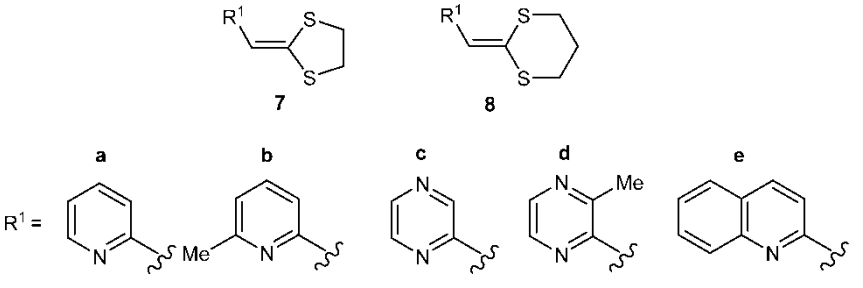


SCHEME 1

on 2-benzylpyridine [9] and 2-(cyanomethyl)pyridine [10, 11]; the latter provides a good illustration of the use of the product in synthesis.

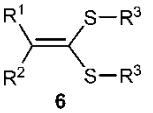


2. Results and discussion

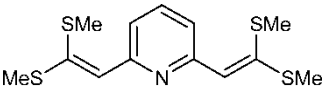
The results of reactions analogous to those reported in reference [9] are shown in table 1. In each case the presence of a singlet at δ *ca* 6.6 in the ^{1}H-NMR spectrum was diagnostic for the olefinic proton.

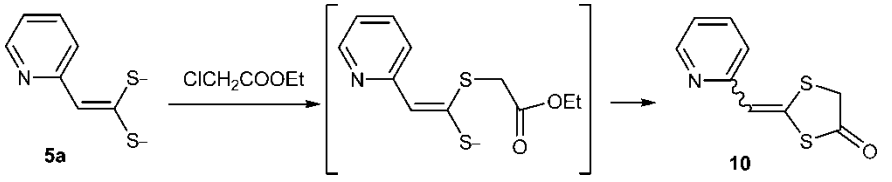
The reaction of 2,6-dimethylpyridine with two equivalents of LDA followed by carbon disulfide and then methyl iodide afforded compounds **6b** (35%) and **9** (45%).

Table 1.



Compd. **6**	R^1	R^2	R^3	Yield %
a	2-Pyridyl	H	Me	85
b	6-Methyl-2-pyridyl	H	Me	35
c	2-Pyrazinyl	H	Me	65
d	2-Quinolinyl	H	$-(CH_2)_2-$	70
e	2-Pyridyl	H	$-(CH_2)_2-$	75

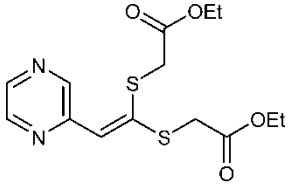




SCHEME 2

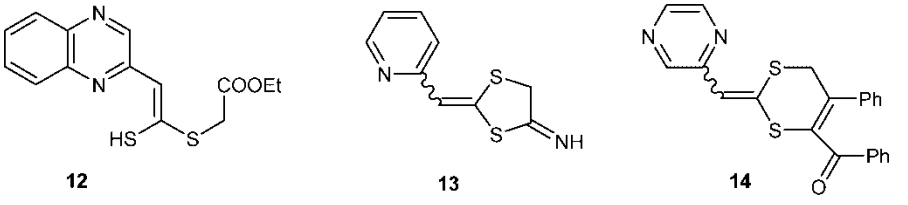
Reactions of the dianion (**5a**) with α-halogenocarbonyl compounds or α-halogenonitriles could lead to cyclic products. Indeed, treatment with an equimolar amount of ethyl chloroacetate gave 2-pyridin-2-ylmethylene-1,3-dithiolan-4-one (**10**), as shown in scheme 2.

On the other hand, a reaction of the dianion derived from 2-methylpyrazine (**1c**) with ethyl chloroacetate gave the dialkylated product (**11**).



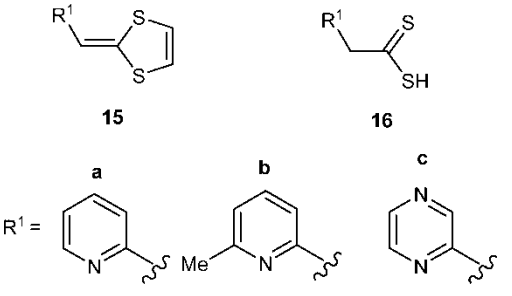
11

Products of other reactions of these and related types are listed below. The ^{1}H NMR spectrum of compound (**12**), from reaction of (**5d**) with ethyl chloroacetate, shows signals at δ 5.9 (1H, s, exchangeable, SH), 6.53 (1H, s, =CH) and 4.08 (2H, s, CH_2) ppm. This tautomer is stabilized by intramolecular hydrogen bonding. The ^{1}H NMR spectra of compounds **10**, **13** and **14** similarly showed singlets corresponding to the olefinic proton and the methylene group. It should be noted that geometrical isomers of compounds (**10**, **13** and **14**) are possible. In each case, the NMR spectra indicated that only one isomer was obtained, but did not determine whether it was *E* or *Z*.



12 **13** **14**

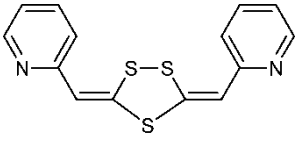
A reaction of the dianion (**5a**, **b**, **c**) with 1,2-dibromoethene could give an alkylidene-dithiolene (**15**), which could have interesting electronic properties.



15 **16**

However, attempted reactions of this type led only to the dithiocarboxylic acids (**16a–c**) arising from hydrolysis of the dianion. The ^{1}H NMR showed 2H singlets at $\delta \approx 2.2$ ppm, corresponding to the methylene group and exchangeable singlets at $\delta \approx 17.2$ ppm, corresponding to the CSSH group.

A reaction of the dianion (**5a**) with aqueous ammonium persulfate gave a compound whose spectroscopic properties corresponded to the structure (**17**). The mass spectrum shows the molecular ion peak at m/z 302 (M^+, 32%) and the ^{1}H NMR spectrum showed a singlet at $\delta \approx 6.48$ ppm diagnostic for the olefinic proton, beside the aromatic protons in the ratio 1:4.



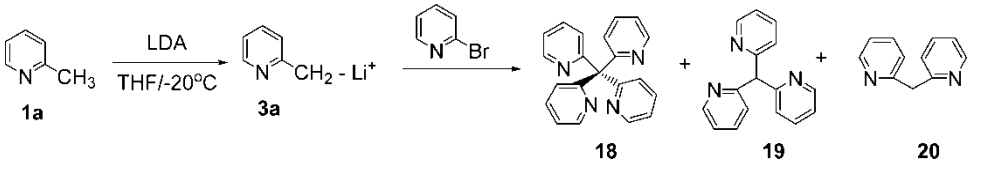
17

When 2-methylpyridine (**1a**) was treated with excess of lithium diisopropylamide (LDA), at low temperature, followed by 2-bromopyridine, the main product was tetra-2-pyridylmethane (**18**) (60%) with only traces of tri-2-pyridylmethane (**19**) and di-2-pyridylmethane (**20**) (scheme 3) [12]. The identity of the main product was established by spectral data as well as elemental analysis. The formation of tetra-2-pyridylmethane (**18**) is easily rationalized: di-2-pyridylmethane (**20**) is more acidic than 2-methylpyridine (**1a**), and is preferentially deprotonated as it is formed; tri-2-pyridylmethane (**19**) is presumably even more acidic, so that the tri-2-pyridylmethyl carbanion predominates in the solution and gives rise to final product (**18**). Matsumoto *et al.* [12] reported the preparation of compound (**18**) using *n*-butyl lithium in different solvents, but we have found that using of LDA is better than *n*-butyl lithium in THF. This compound (**18**) is of considerable interest as a complexing agent [13–16].

2.1 *Experimental*

Melting points are uncorrected. IR spectra were recorded on a Perkin–Elmer 1710 FTIR spectrometer as KBr disks. NMR spectra were recorded on a Bruker AC300 spectrometer at 200 MHz for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard, unless otherwise recorded. Mass spectra were obtained on a Finnigan 4500 spectrometer using electron impact (EI), or chemical ionization (CI) using ammonia at Salford University, UK. Elemental analysis was performed at Manchester University, UK. 2-Methylpyridine (**1a**), 2,6-dimethylpyridine (**1b**), 2-methylpyrazine (**1c**), 2-methylquinoxaline (**1d**) and diisopropylamine are commercially available.

2.1.1 Reaction of methylazines (1a,b,c,f) with lithium diisopropylamide (LDA), carbon disulfide and alkyl halides. General procedure. A dry, 500 ml three-necked flask was equipped with a mechanical stirrer, a low temperature thermometer, and a pressure-equalizing



SCHEME 3

funnel, and furnished with an atmosphere of dry argon. The flask was charged with dry THF (100 ml) and diisopropylamine (1.91 g, 18.9 mmol) and the mixture was cooled to −65 °C. *n*-Butyl lithium (ca 1.4 M in hexane, 18.9 mmol) was added, the mixture was stirred for about 20 min at < −20 °C. A methylazine (8.6 mmol) was added and the resulting orange suspension was stirred for 45 min, then carbon disulfide was added dropwise during the next 10 min and stirring was continued for 1 h. The appropriate halo compound was added dropwise, the temperature was allowed to rise to room temperature, and stirring at room temperature was continued for 2 h. Wet diethyl ether (50 ml) was added. The solvents were removed by rotary evaporation, and the residue was dissolved in chloroform (100 ml). The solution was washed with 0.5M H_2SO_4 (50 ml), H_2O (50 ml) and brine (50 ml). The aqueous layer was basified with 4 M NaOH and extracted with chloroform (50 ml). The combined organic solutions were washed with brine (50 ml), dried over magnesium sulfate and concentrated by rotatory evaporator. The residue was subjected to column chromatography (silica gel, light petroleum/EtOAc (4:1)).

2.1.2 2-(2,2-Bis-methylsulfanylvinyl)pyridine (6a). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and methyl iodide (2.5 g, 17.6 mmol); red semisolid; yield 85%; $R_f = 0.32$; IR: (υ_{max}, cm^{-1}) 3048(C-H Ar), 2992, 2918 (C-H Ali.), δ_H 2.39 (s, 3H, SMe), 2.41 (s, 3H, SMe), 6.54 (s, 1H, CH), 7.01 (dt, 1H, $J = 8$, 2 Hz, Ar), 7.56 (m, 2H, Ar), 8.54 (m, 1H, Ar) MS: m/z(CI) 198 (M^++1). Anal. Calcd for $C_9H_{11}NS_2$: C, 54.78; H, 5.62; N, 7.10; S, 32.50. Found: C, 54.6; H, 5.7; N, 9.8; S, 32.6%.

2.1.3 2-(2,2-Bis-methylsulfanylvinyl)-6-methylpyridine (6b) and 2,6-bis-(2,2-bis-methyl sulfanyl-vinyl)pyridine (9). These compounds were prepared using the method described above using 2,6-dimethylpyridine (**1b**) (0.92 g, 8.6 mmol) and methyl iodide (5 g, 35.2 mmol), **6b**, $R_f = 0.62$, yield 35%; mp 105 °C. IR: (υ_{max}, cm^{-1}), 3048 (C-H Ar), 2990, 2915 (C-H Ali.), 1622 (C=C) δ_H 2.29(s, 3H, CH_3), 2.32(s, 3H, SCH_3), 2.43(s, 3H, SCH_3), 6.48(s, 1H, CH), 7.01(d, 1H, Ar, $J = 7.8$ Hz), 7.29(d, 1H, Ar, $J = 7.7$ Hz), 7.40(t, 1H, Ar, $J = 7.8$ Hz). MS: m/z(EI) 211 (M^+, 15%), 196 (M-15, 72%). Anal. Calcd for $C_{10}H_{13}NS_2$: C, 56.83; H, 6.20; N, 6.63; S, 30.34. Found: C, 56.6; H, 6.0; N, 6.7; S, 30.2%. **9**, $R_f = 0.26$, yield 45%; mp 95 °C. IR: (υ_{max}, cm^{-1}), 3046(C-H Ar), 2993, 2925 (C-H Ali.), 1622 (C=C) δ_H 2.39(s, 3H, SCH_3), 2.43(s, 3H, SCH_3), 2.53(s, 3H, SCH_3), 2.64(s, 3H, SCH_3), 6.59(s, 2H, 2CH), 6.94(t, 1H, Ar, J =7.5 Hz), 7.42(d, 2H, Ar, J =7.5 Hz). MS: m/z(EI) 345 (M^+). Anal. Calcd for $C_{13}H_{17}NS_4$: C, 49.48; H, 5.43; N, 4.44; S, 40.65. Found: C, 49.3; H, 5.2; N, 4.5; S, 40.5%.

2.1.4 2-(2,2-Bismethylsulfanyl-vinyl)-pyrazine (6c). This compound was obtained by the method described above using 2-methylpyrazine (**1c**) (0.81 g, 8.6 mmol) and methyl iodide (2.5 g, 17.6 mmol). Orange plates, yield 65%; mp 58–60 °C $R_f = 0.5$ (EA/PE, 2 : 1). IR: (υ_{max}, cm^{-1}) 3048 (C-H Ar), 2992, 2918 (C-H Ali.), δ_H 2.46(s, 3H, SMe), 2.47 (s, 3H, SMe), 6.49 (s, 1H, CH), 8.24 (d, 1H, $J = 2.7$ Hz, Ar), 8.50(d, 1H, $J = 1.7$ Hz, Ar), 8.67 (dd, 1H, $J = 2.7$, 1.7 Hz, Ar). MS: m/z(EI) 198 (M^+, 60%), 183 (M-15, 100%). Anal. Calcd for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.08; N, 14.13; S, 32.34. Found: C, 48.6; H, 5.2; N, 14.3; S, 32.5%.

2.1.5 2-[1,3]Dithiolan-2-ylidenemethylpyridine (6e). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and 1,2-dibromoethane (1.62 g, 8.6 mmol), yellow crystals; $R_f = 0.43$: yield 75%; mp 95-7 °C. IR:

(υ_{max}, cm^{-1}) 3048 (C-H Ar), 2990, 2915 (C-H Ali.), δ_H 3.29 (t, 2H, CH_2), 3.41 (t, 2H, CH_2), 6.68 (s, 1H, CH), 6.95 (m, 1H, Ar), 7.02 (dd, 1H, Ar, $J = 7.9$, 1.3 Hz), 7.52 (dt, 1H, Ar, $J = 7.7$, 2.2 Hz) 8.59 (dt, 1H, Ar, $J = 5$, 1 Hz) MS: m/z(CI) 196 ($M^+ + 1$). Anal. Calcd for $C_9H_9NS_2$: C, 55.35; H, 4.64; N, 7.17; S, 32.84. Found: C, 55.2; H, 4.7; N, 7.3; S, 32.7%.

2.1.6 2-Pyridin-2-ylmethylene-[1,3]dithiolan-4-one (10). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and ethyl chloroacetate (0.78 g, 8.6 mmol), red powder; $R_f = 0.56$; yield 70%; mp 115-7 °C. IR: (υ_{max}, cm^{-1}) 3048 (C-H Ar), 2990, 2915 (C-H Ali.), 1727 (C=O), 1638 (C=C) δ_H 3.81 (s, 2H, CH_2), 6.75 (s, 1H, CH), 7.02 (m, 1H, Ar), 7.33 (dd, 1H, Ar, $J = 8.9$, 1.3 Hz), 7.43 (dt, 1H, Ar, $J = 7.7$, 2.1 Hz) 8.59 (dt, 1H, Ar, $J = 4.7$, 1.2 Hz) MS: m/z(EI) 209 (M^+, 98%), 135 (M-74, 100%). Anal. Calcd for $C_9H_7NOS_2$: C, 51.65; H, 3.37; N, 6.69; S, 30.64. Found: C, 51.4; H, 3.4; N, 6.8; S, 30.7%.

2.1.7 Ethyl (1-Ethoxycarbonylmethylsulfanyl-2-pyrazin-2-yl-vinylsulfanyl)acetate (11). This compound was obtained by the method described above using 2-methylpyrazine (**1c**) (0.81 g, 8.6 mmol) and ethyl chloroacetate (1.56 g, 17.2 mmol), red semisolid, yield 60%; $R_f = 0.2$ (EA/PE, 1:3). IR: (υ_{max}, cm^{-1}) 3045 (C-H Ar), 2991, 2915 (C-H Ali.), δ_H 1.03–1.07 (t, 3H, Me), 1.10 (s, 3H, Me), 4.01 (2q, 4H, $2CH_2$), 6.96 (s, 1H, CH), 8.21 (d, 1H, Ar, $J =$ 2.8 Hz), 8.42 (dd, 1H, Ar, $J = 2.8$, 1.6 Hz), 8.73 (d, 1H, Ar, $J = 1.6$ Hz). MS: m/z(EI) 342 (M^+, 60%), accurate mass, calcd. 342.07028, found 342.0702. Anal. Calcd for $C_{14}H_{18}N_2O_4S_2$: C, 49.10; H, 5.30; N, 8.18; S, 18.73. Found: C, 48.9; H, 5.2; N, 18.3; S, 18.5%.

2.1.8 Ethyl (1-mecapto-2-quinoxalin-2-yl-vinylsulfanyl)-acetate (12). This compound was obtained by the method described above using 2-methylquinoxaline (**1f**) (1.24 g, 8.6 mmol) and ethyl chloroacetate (1.56 g, 17.2 mmol), orange crystals, mp. 170-2 °C, yield 60%; $R_f = 0.68$ (EA/PE, 1:1). IR: (υ_{max}, cm^{-1}) 3045 (C-H Ar), 2991, 2915 (C-H Ali.), 1721 (C=O), 1609 (C=C), δ_H 1.29 (t, 3H, Me, $J = 7.2$ Hz), 4.08 (s, 2H, CH_2), 4.22 (q, 2H, CH_2 $J = 7.2$ Hz), 6.53 (s, 1H, CH), 7.39 (t, 1H, Ar, $J = 8.5$ Hz),7.53 (t, 1H, Ar, $J = 7.2$ Hz), 7.775 (d, 1H, Ar, $J = 8.4$ Hz), 8.265 (d, 1H, Ar, $J = 7.4$ Hz), 8.65 (s, 1H, Ar), 15.9 (s, exch., 1H, SH), MS: m/z(EI) 306 (M^+), Anal. Calcd for $C_{14}H_{14}N_2O_2S_2$: C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found: C, 55.02; H, 4.62; N, 8.95; S, 20.80%.

2.1.9 2-Pyridin-2-ylmethylene-[1,3]dithiolan-4-ylideneamine (13). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and chloroacetonitrile (0.65 g, 8.6 mmol), deep red powder; light petroleum/EtOAc (1:1); yield 65%; mp 137-9 °C. IR: (υ_{max}, cm^{-1}) 3260 (NH), 3048 (C-H Ar), 2990, 2915 (C-H Ali.), 1622 (C=C) δ_H 4.1 (s, 2H, CH_2), 6.46 (s, 1H, CH), 7.02 (d, 1H, Ar, $J = 7.9$ Hz), 7.33 (dd, 1H, Ar, $J = 8.7$, 1.2 Hz), 7.52 (dt, 1H, Ar, $J = 7.7$, 2.2 Hz) 8.59 (dt, 1H, Ar, 4.7 Hz) MS: m/z(EI) 209 (M^+), 136, 93 (100%). Anal. Calcd for $C_9H_8N_2S_2$: C, 51.89; H, 3.87; N, 13.45; S, 30.79. Found: C, 51.6; H, 3.6; N, 13.6; S, 30.6%.

2.1.10 4-Benzoyl-5-phenyl-2-pyrazin-2-ylmethylene-6H-[1,3]dithiine (14): This compound was obtained by the method described above using 2-methylpyrazine (**1c**) (0.81 g, 8.6 mmol) and pheacylbromide (3.42 g, 17.2 mmol), orange powder, yield 70%; mp. 65-6 °C $R_f = 0.13$ (EA/PE, 1:4). IR: (υ_{max}, cm^{-1}) 3045(C-H Ar), 2991, 2915 (C-H Ali.), δ_H 4.29

(s, 2H, CH_2), 6.99 (s, 1H, CH), 7.04 (m, 10H, Ar), 8.21 (d, 1H, Ar, $J = 2.8$ Hz), 8.42 (dd, 1H, Ar, $J = 2.8, 1.6$ Hz), 8.73 (d, 1H, Ar, $J = 1.6$ Hz). MS: m/z(EI) 388 (M^+, 60%), 283 (M-105), 105 (100%) accurate mass, Calcd. 388.0704, found 388.0706. Anal. Calcd for $C_{22}H_{16}N_2OS_2$: C, 68.01; H, 4.15; N, 7.21; S, 16.51. Found: C, 67.8; H, 4.2; N, 7.3; S, 16.6%.

2.1.11 Pyridin-2-yl-dithioacetic acid (16a). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and 1,2-dibromoethene (8.6 mmol), brown powder (light petroleum/EtOAc (1:1)); yield 65%; mp >250 °C. IR: (υ_{max}, cm^{-1}), 3048 (C-H Ar), 2990, 2915 (C-H Ali.), 1622 (C=C) δ_H 2.2 (s, 2H, CH_2), 7.33 (t, 1H, Ar, $J = 4.9$ Hz), 7.02(d, 1H, Ar, $J = 7.9$ Hz), 7.43 (t, 1H, Ar, $J = 7.7$ Hz) 8.59 (dt, 1H, Ar, $J = 4.7, 1.2$ Hz), 17.2 (exch., 1H, SH) MS: m/z (EI) 169 (M^+). Anal. Calcd for $C_7H_7NS_2$: C, 49.67; H, 4.17; N, 8.27; S, 37.89. Found: C, 49.5; H, 4.0; N, 8.4; S, 37.6%.

2.1.12 (6-Methylpyridin-2-yl)-dithioacetic acid (16b). The reaction was carried out as described above using 2,6-dimethylpyridine (**1b**) (0.92 g, 8.6 mmol) and 1,2-dibromoethene (8.6 mmol), red crystals, $R_f = 0.62$, yield 60%; mp >250 °C. IR: (υ_{max}, cm^{-1}), 3046 (C-H Ar), 2991, 2918 (C-H Ali.), 1622 (C=C) δ_H 2.14 (s, 2H, CH_2), 2.55 (s, 3H, CH_3), 6.81 (d, 1H, Ar, $J = 7.4$ Hz), 6.91 (d, 1H, Ar, $J = 7.4$ Hz), 7.62 (t, 1H, Ar, $J = 7.4$ Hz), 17.21 (s, exch., 1H, SH). MS: m/z (EI) 183 (M^+, 20%), 150 (M-33, 50%), 107 (M-76, 100%). Anal. Calcd for $C_8H_9NS_2$: C, 52.42; H, 4.95; N, 7.64; S, 34.99. Found: C, 52.6; H, 5.0; N, 7.7; S, 34.8%.

2.1.13 Pyrazin-2-yl-dithioacetic acid (16c). This compound was obtained by the method described above using 2-methylpyrazine (**1c**) (0.81 g, 8.6 mmol) and 1,2-dibromoethene (8.6 mmol), violet powder, yield 70%; mp. >250 °C $R_f = 0.2$ (EA/PE, 3 : 1). IR: (υ_{max}, cm^{-1}) 3045 (C-H Ar), 2991, 2915 (C-H Ali.), δ_H 2.26 (s, 2H, CH_2), 8.21 (d, 1H, Ar), 8.42 (dd, 1H, Ar, $J = 2.7, 1.7$ Hz), 8.73 (d, 1H, Ar, $J = 2.7$ Hz), 17.1 (s, exch. 1H, SH). MS: m/z(EI) 170 (M^+, 50%), Anal. Calcd for $C_6H_6N_2S_2$: C, 42.33; H, 3.55; N, 16.45; S, 37.67. Found: C, 42.1; H, 3.3; N, 16.3; S, 37.5%.

2.1.14 Preparation of compound (17). This compound was prepared using the method described above using 2-methylpyridine (**1a**) (0.8 g, 8.6 mmol) and ammonium persulfate (8.6 mmol), deep violet fine crystals; $R_f = 0.3$; yield 72%; mp 150-1 °C. IR: (υ_{max}, cm^{-1}) 3072, 3045 (C-H Ar), 1622 (C=C) δ_H 6.48 (s, 1H, CH), 7.02 (m, 1H, Ar), 7.33 (dd, 1H, Ar, $J = 8.9, 1.2$ Hz), 7.53 (dt, 1H, Ar, $J = 7.7, 2.1$ Hz) 8.59 (dt, 1H, Ar, $J = 4.7, 1.2$ Hz) MS: m/z (EI) 302 (M^+, 32%), 167 (M-135, 77%), 135 (M-167, 55%), 78 (100%), 57 (32%). Anal. Calcd. for $C_{14}H_{10}N_2S_3$: C, 55.60; H, 3.33; N, 9.26; S, 31.81. Found: C, 55.4; H, 3.1; N, 9.4; S, 31.6%.

2.1.15 Tetra-2-pyridylmethane (18). A dry, 500 ml three-necked flask was equipped with a mechanical stirrer, a low temperature thermometer, and a pressure-equalizing funnel, and furnished with an atmosphere of dry argon. The flask was charged with dry THF (100 ml) and diisopropylamine (1.91 g, 18.9 mmol) and the mixture was cooled to −65 °C. *n*-Butyl lithium (ca 1.4 M in hexane, 18.9 mmol) was added, the mixture was stirred for about 20 min at <−20 °C. 2-Methylpyridine (**1a**) (0.8 g, 8.6 mmol) was added and the resulting orange suspension was stirred for 45 min. and 2-bromopyridine (3.72 g, 2.28 mmole), was added dropwise, the temperature was allowed to rise to room temperature, and stirring at room temperature was continued for 2 h. Wet diethyl ether (50 ml) was added. The solvents were removed

by rotary evaporation, and the residue was dissolved in chloroform (100 ml). The solution was washed with 0.5M H_2SO_4 (50 ml), H_2O (50 ml) and brine (50 ml). The aqueous layer was basified with 4 M NaOH and extracted with chloroform (50 ml). The combined organic solutions were washed with brine (50 ml), dried over magnesium sulphate and concentrated by rotatory evaporator. The residue was subjected to column chromatography (silica gel, light petroleum/EtOAc (4:1). Brown powder; yield 60%; mp 180 °C (decomp.). IR: (υ_{max}, cm^{-1}) 3048 (C-H, Ar), 1622 (C=C) δ_H ($CDCl_3$); 7.02 (d, Ar, $J = 7.9$ Hz), 7.33 (t, Ar, $J = 4.9$ Hz), 7.53 (t, Ar, $J = 7.7$ Hz) 8.59 (dt, Ar, $J = 4.7$, 1.2 Hz), δ_C ($CDCl_3$); 158.9, 149.8, 136.4, 123.4, 121.1, 65.3, MS: m/z(EI) 324 (M^+), 246 (M-78, 100%). Anal. Calcd for $C_{21}H_{16}N_4$: C, 77.74; H, 4.97; N, 17.28. Found: C, 77.6; H, 4.7; N, 17.4%.

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