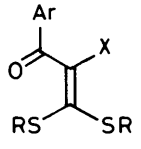
Polarised Ketene Dithioacetals. Part 50.[1] Reactions of α-Aroyl-α-bromoketene Dithioacetals with Hydrazine Hydrate: Formation of Rearranged Pyrazoles

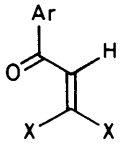
Gurdeep Singh, Hiriyakkanavar Ila,* and Hiriyakkanavar Junjappa*
Department of Chemistry, North-Eastern Hill University, Bijni Complex, Shillong 793 003, Meghalaya, India

The reactions of α-aroyl-α-bromoketene dithioacetals (**2a**—**c**) with hydrazine hydrate yields unexpected pyrazoles, *i.e.* 3(5)-aryl-5(3)-4-bis(alkylthio)pyrazoles (**7**), 3(5)-arylpyrazoles (**8**), and 4-amino-5(3)-alkylthiopyrazoles (**9**) in varying yields. The corresponding *S*-ethyl-α-bromoketene dithioacetal (**2d**) gave only the bis(ethylthio)pyrazole (**7d**) and 4-amino-4(3)-ethylthiopyrazole (**9d**) under similar conditions. The reactions of cyclic α-bromo ketene dithioacetals (**2e**—**g**) with hydrazine hydrate on the other hand afforded only the [1,4]dithiinopyrazole derivatives (**7e**—**g**) in high yields. The probable mechanisms for the formation of the pyrazoles (**7**)—(**9**) have been suggested.

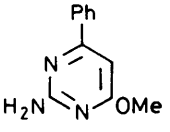
We have recently[2] reported the synthesis of novel α-aroyl-α-bromoketene dithioacetals (**2**) by direct bromination of the corresponding α-aroylketene dithioacetals (**1**) with *N*-bromosuccinimide. The α-bromo dithioacetals (**2**) were shown to undergo ready displacement with copper(I) cyanide and copper(I) arenethiolates to give the corresponding α-aroyl-α-cyano- (**3**) and α-aroyl-α-arylthio-(**4**) ketene dithioacetals in good yields. On the other hand, when compound (**2a**; Ar = Ph, R = Me) was treated with morpholine, the products isolated were found to be either the debrominated dithioacetal (**1a**; Ar = Ph, R = Me) or the corresponding dimorpholinoacetal (**5**; Ar = Ph) and no product formed by displacement of bromine by morpholine was detected in the reaction mixture. Similarly, reaction of compound (**2a**) with guanidine nitrate in the presence of sodium methoxide in refluxing methanol yielded only the debrominated pyrimidine (**6**).[3,†] However, when compounds (**2**) were treated with hydrizine hydrate, the pyrazoles (**7**), (**8**), and (**9**) with unexpected structural features were obtained in varying yields (Scheme 1). The structural assignments and the probable mechanisms of the formation of these pyrazoles are described in this paper.



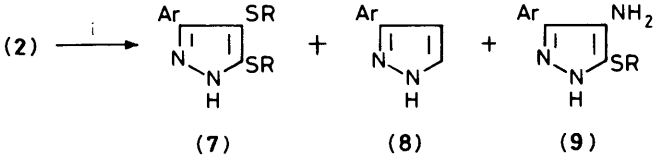
(**1**) X = H
(**2**) X = Br
(**3**) X = CN
(**4**) X = SAr



(**5**) X = morpholino

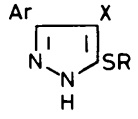


(**6**)



(**7**) (**8**) (**9**)

(**2**),(**7**)—(**9**) **a**; Ar = Ph, R = Me
b; Ar = *p*-ClC$_6$H$_4$, R = Me
c; Ar = *p*-MeC$_6$H$_4$, R = Me
(**2**),(**7**),(**9**) **d**; Ar = Ph, R = Et



(**10**) X = Br
(**11**) X = H

Scheme 1. *Reagents:* i, N_2H_4, EtOH

Results and Discussion

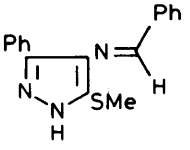
When compound (**2a**) was refluxed for 2 h with excess of hydrazine hydrate in ethanol, the reaction mixture after work-up showed (t.l.c.) the formation of three products, which were isolated by column chromatography and characterised as the pyrazoles (**7a**) (42%), (**8a**) (10%), and (**9a**) (30%). Neither the 4-bromopyrazole (**10**; Ar = Ph, R = Me) nor the corresponding debrominated pyrazole (**11**) was detected in the reaction mixture. The structural assignment for products (**7a**)—(**9a**) was made on the basis of their spectral and analytical data. The pyrazole (**7a**) showed the molecular-ion peak at *m/z* 236 (M^+) and analysed for $C_{11}H_{12}N_2S_2$. Its i.r. spectrum (KBr) exhibited a broad band at 3 175 cm^{-1} (NH) and medium intensity peaks at 1 582, 1 546, 1 490, and 1 464 cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) of compound (**7a**) confirmed the presence of two methylthio groups which appeared at δ 2.20 (s, 3 H) and 2.50 (s, 3 H) along with the aromatic protons at δ 7.15—7.46 (3 H) and δ 7.61—7.82 (m, 2 H). The low-field broad singlet at δ 12.15 (1 H, exchangeable with D_2O) was assigned to the pyrazole NH proton. The ^{13}C n.m.r. data (Experimental section) further confirmed the structural assignment for compound (**7a**).

The pyrazole (**8a**) is reported in literature[4,5] and was confirmed by comparison of its spectral data with those of an authentic sample (mixed m.p. and superposable i.r.).

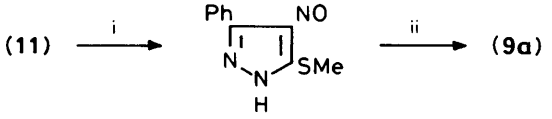
The structure of the third compound, characterised as 4-amino-5(3)-methylthio-3(5)-phenylpyrazole (**9a**), was also established by its spectral and analytical data. Its elemental analysis was in accord with the molecular formula $C_{10}H_{11}N_3S$, and mass spectral data showed a molecular-ion peak at *m/z* 205

† The pyrimidine (**6**) had previously been obtained by the reaction of compound (**1a**) with guanidine nitrate under identical conditions (S. M. S. Chauhan and H. Junjappa, *Synthesis*, 1974, 880).

(100%). The presence of an amino group in compound (**9a**) was supported by its i.r. spectrum (KBr), which exhibited broad bands in the range to 3 150—3 500 cm^{-1} due to free and H-bonded NH stretching vibrations,[6] besides sharp peaks at 1 605 (δ_{NH_2}) and 1 590 ($\nu_{C=N}$) cm^{-1}. The ^1H n.m.r. spectrum of compound (**9a**) ($CDCl_3$) showed a singlet at δ 2.2 (3 H, SMe) and a multiplet due to aromatic protons at δ 7.67—7.23 (5 H), while the two amino and ring NH protons appeared as a broad singlet at δ 6.5 (3 H, exchangeable with D_2O).[7,8] The ^{13}C n.m.r. spectrum (Experimental section) of compound (**9a**) was also in agreement with the assigned structure. Reaction of compound (**9a**) with benzaldehyde yielded the Schiff's base (**12**), which further confirmed the presence of a primary amino group. The position of this amino group in compound (**9a**) was ascertained by its independent synthesis from compound (**11**) (Scheme 2).



(**12**)

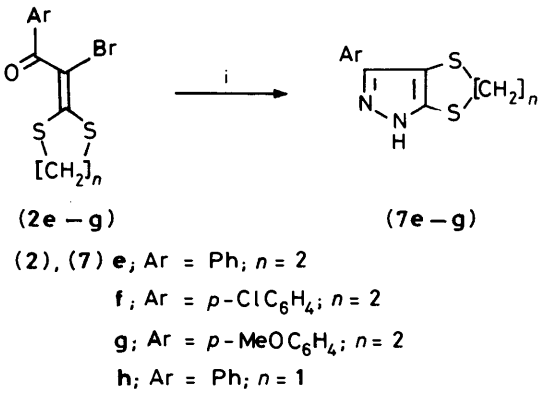


(**13**)

Scheme 2. *Reagents:* i, NOCl, pyridine; ii, Zn–AcOH, EtOH

Thus, nitrosation of (**11**) with nitrosyl chloride gave the corresponding 4-nitrosopyrazole (**13**) in 88% yield,[9] which on reduction with zinc and acetic acid afforded the 4-amino-pyrazole, found to be identical with compound (**9a**) (superposable i.r. and n.m.r. spectra, and mixed m.p.).

The other substituted bromoketene dithioacetals (**2b**) and (**2c**) similarly afforded the corresponding pyrazoles (**7b, c**), (**8b, c**), and (**9b, c**) in comparable yields. However, the corresponding *S*-ethyl acetal (**2d**) gave only the pyrazoles (**7d**) and (**9d**) under identical conditions, while compound (**8a**) could not be detected in the reaction mixture. Interestingly, when the cyclic bromo-acetal (**2e**) was treated with hydrazine hydrate under similar conditions, the corresponding fused [1,4]dithiinopyrazole (**7e**) was isolated in 76% yield (Scheme 3). Similarly, fused pyrazoles (**7f**) and (**7g**) were obtained from the respective dithioacetals (**2f**) and (**2g**) in high yields. However, under these conditions the corresponding 1,3-dithietane (**2h**; Ar = Ph; n = 1) did not give the expected pyrazole (**7h**; Ar = Ph; n = 1), and yielded only intractable tar.



(**2e – g**) (**7e – g**)

(**2**), (**7**) **e**; Ar = Ph; n = 2

f; Ar = *p*-ClC_6H_4; n = 2

g; Ar = *p*-$MeOC_6H_4$; n = 2

h; Ar = Ph; n = 1

Scheme 3. *Reagents:* i, N_2H_4, EtOH

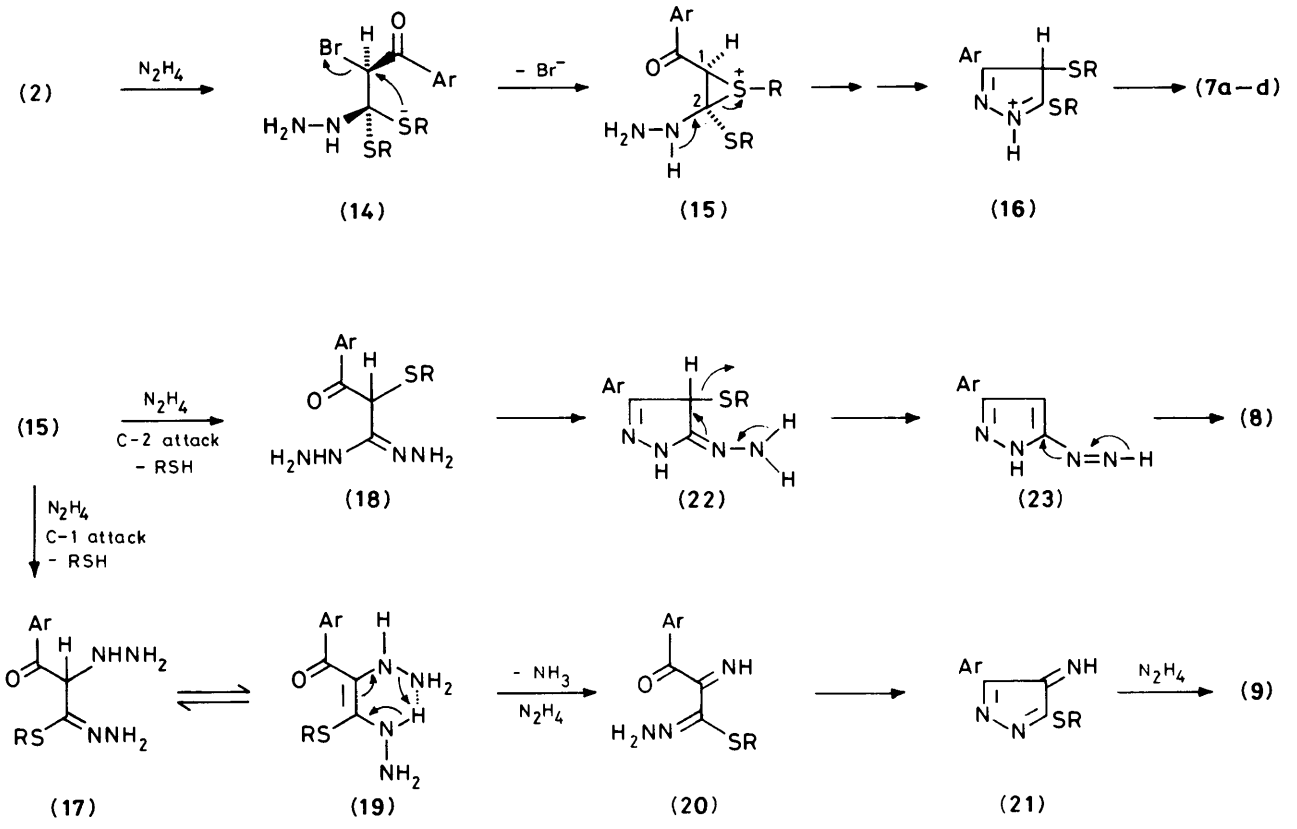
Mechanism

The mechanism governing the formation of the unexpected pyrazoles (**7**), (**8**), and (**9**) from the bromoketene dithioacetals (**2**) appears to involve interesting rearrangements. Experiments monitoring the reactions of compound (**2a**) with hydrazine hydrate at different time intervals, together with product analysis, showed that the formation of all three pyrazoles follows independent pathways from the same common intermediate and that they are not derived from each other. The probable mechanism proposed for these transformations is depicted in Scheme 4. Thus, the formation of episulphonium ion intermediate (**15**)* *via* the sulphur-assisted elimination of bromine in the Michael adduct (**14**) appears to be the first such step from which the various pyrazoles could be obtained by different sequences of reactions. In one of the pathways intermediate (**15**) can undergo intramolecular ring opening accompanied by a 1,2-alkylthio shift and concurrent cyclisation to give the corresponding 4,5(3)-bis(alkylthio)pyrazoles (**7a—d**) *via* iminum ion (**16**). The intermediate (**15**) could also be attacked by a second molecule of hydrazine hydrate either at C-1 or at C-2 followed by elimination of alkyl mercaptan leading to intermediates (**17**) and (**18**) respectively. The intermediate (**17**) can undergo elimination of ammonia *via* tautomer (**19**)† to give hydrazone (**20**), which on subsequent cyclisation [to (**21**)] and reduction with hydrazine afford the 4-amino-pyrazole (**9**) as one of the products. Similarly, the intermediate (**18**) obtained by attack of hydrazine at C-2 can undergo ready cyclisation [to (**22**)] and elimination of the methylthio group to give diazopyrazole intermediate (**23**), which on subsequent reductive elimination of nitrogen affords 4,5-unsubstituted pyrazoles (**8**) in low yields. Apparently, it appears that the lower yields of compounds (**8**) are due to preferential attack of hydrazine hydrate at the C-1 position than at the comparatively more hindered C-5 position in the episulphonium ion intermediate (**15**). The steric factor responsible for the low yields of compounds (**8**) was further established when the bis(ethylthio)-bromoacetal (**2d**) failed to give compound (**8a**) under identical conditions. The fact that the cyclic bromo dithioacetals (**2e—g**) react with hydrazine hydrate to give only the corresponding [1,4]dithiinopyrazoles (**7e—g**), and that the other pyrazoles, as obtained in the case of dithioacetals (**2a—d**), were not formed, suggests that the formation of compounds (**7e—g**), does not involve the formation of strained episulphonium ion intermediates (**15e—g**; R = $[CH_2]_2$), and instead appears to proceed by concerted 1,2-alkylthio migration and elimination of bromine.

In conclusion, the reaction of α-bromoketene dithioacetals (**2**) with hydrazine hydrate affords hitherto unknown pyrazoles (**7**), (**9**), and known pyrazoles (**8**), *via* interesting transformations.

* 1,2-Arylthio migration *via* an episulphonium intermediate has recently been reported in thermal decomposition of some pyrazoline derivatives (M. Hamaguchi, S. Myazaki, and T. Nagai, *J. Chem. Soc., Chem. Commun.*, 1983, 12) and 2,2-bis(phenylthio)ethanol (P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1055).

† The evolution of ammonia from the intermediate (**20**) is similar to that observed in the reaction of hydrazine hydrate with phenacyl bromide (S. Hauptmann, M. Kluge, K.-D. Seidig, and H. Wilde, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 688) and the elimination of aniline from the dihydrazinoalkene intermediate during osazone formation (H. O. House, 'Modern Synthetic Reactions, W. A. Benjamin, 1972, p. 239); A. Hassner and P. Catsoulacos, *Tetrahedron Lett.*, 1967, 489.



Scheme 4.

Experimental

M.p.s were determined on a Thomas Hoover m.p. apparatus and are uncorrected. I.r. spectra were run on a Perkin-Elmer 297 spectrophotometer, while the ^1H n.m.r. spectra were recorded at 90 MHz on a Varian EM-390 spectrometer and the chemical-shift values are expressed as δ-values (p.p.m.) downfield from tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded either on a Varian CFT-20 (20 MHz) instrument or on a Bruker WH-270 (67.89 MHz) instrument. T.l.c. (silica gel B.D.H.) was used for monitoring the reactions with EtOAc–C_6H_6 (1:10) as developing solvent.

Starting Materials.—All the α-aroylketene dithioacetals (**1a**—**h**) used in the present study were prepared according to the method reported earlier.[10] The known α-bromo dithioacetals (**2a**—**d**) and the unknown α-bromo dithioacetals (**2e**—**h**) were prepared from the respective compounds (**1a**—**h**) as reported in ref. 2.

2-(α-*Bromophenacylidene*)-1,3-*dithiole* (**2e**) (98%) was isolated as light yellow crystals (from hexane), m.p. 84—85 °C; $\nu_{max.}$(KBr) 1 603 and 1 595 cm^{-1}: $\delta_H(CCl_4)$ 3.27—3.65 (2 t, 4 H, $S[CH_2]_2S$), 7.23—7.45 (m, 3 H, ArH), and 7.59—7.79 (m, 2 H, ArH) (Found: C, 44.2; H, 3.3. $C_{11}H_9BrOS_2$ requires C, 43.86; H, 2.99%); *m/z* 299, 301 (M^+).

2-(α-*Bromo-p-chlorophenacylidene*)-1,3-*dithiole* (**2f**) (96%) was isolated as light yellow crystals (from hexane), m.p. 112—113 °C; $\nu_{max.}$(KBr) 1 605 and 1 592 cm^{-1}; $\delta_H(CCl_4)$ 3.38—3.67 (2 t, 4 H, $S[CH_2]_2S$), and 7.39—7.63 (dd, 4 H, ArH) (Found: C, 39.4; H, 2.6. $C_{11}H_8BrClOS_2$ requires C, 39.35; H, 2.38%).

2-(α-*Bromo*-p-*methoxyphenacylidene*)-1,3-*dithiole* (**2g**) 98%) was isolated as light yellow crystals (from hexane), m.p. 130—131 °C; $\nu_{max.}$(KBr) 1 608 and 1 595 cm^{-1}; $\delta_H(CDCl_3)$ 3.24 (2 t, 4 H, $S[CH_2]_2S$), 3.78 (s, 3 H, OMe), and 6.88—7.85 (dd, 4 H, ArH) (Found: C, 43.4; H, 2.9. $C_{12}H_{11}BrO_2S_2$ requires C, 43.51; H, 3.32%).

2-(α-*Bromophenacylidene*)-1,3-*dithietane* (**2h**) (90%) was isolated as light yellow crystals (from hexane), m.p. 73—74 °C; $\nu_{max.}$(KBr) 1 603 and 1 595 cm^{-1}; $\delta_H(CDCl_3)$ (3.92 (s, 2 H, SCH_2S), 7.2—7.48 (m, 3 H, ArH), and 7.59—7.8 (m, 2 H, ArH) (Found: C, 41.6; H, 2.5. $C_{10}H_7BrOS_2$ requires C, 41.82; H, 2.43%).

General Procedure for the Reaction of α-*Aroyl*-α-*bromoketene Dithioacetals* (**2a**—**h**) *with Hydrazine Hydrate.*—To a solution of compound (**2a**) (3.03 g, 0.01 mol) in absolute ethanol (25 ml) was added hydrazine hydrate (8 ml; 99%) and the reaction mixture was refluxed for 2 h, till the starting material disappeared completely (t.l.c.). The reaction mixture was then poured into water (100 ml), extracted with chloroform (2 × 100 ml), and the combined extracts were washed with water (2 × 70 ml), dried (Na_2SO_4), and evaporated to give a viscous oil, which on column chromatography on silica gel with hexane–ethyl acetate (5:1) as eluant first gave 4,5(3)-*bis*(*methylthio*)-3(5)-*phenylpyrazole* (**7a**) (1.0 g, 42%) as a white solid (from chloroform–hexane), m.p. 130—131 °C; $\delta_C(CDCl_3$; 67.89 MHz) 15.50 (q, SMe), 19.22 (q, SMe), 109.8 (s, C-4), 127.53, 128.71, 128.93, and 129.77 (arom C), 147.49 [s, C-3(5)], and 150.78 [s, C-5(3)] (Found: C, 56.1; H, 4.9; N, 12.0. $C_{11}H_{12}N_2S_2$ requires C, 55.93; H, 5.08; N, 11.86%); *m/z* 236 (M^+). The i.r. and ^1H n.m.r. spectral data are described in the text. Further elution with hexane–ethyl acetate (7:3) yielded 3-phenylpyrazole (**8a**) (0.15 g, 10%) as a white solid (from hexane), m.p. 72—73 °C (lit.,[4] 74—75 °C).

Subsequent elution with hexane–ethyl acetate (1:1) afforded 4-*amino*-5(3)-*methylthio*-3(5)-*phenylpyrazole* (**9a**) (0.61 g, 30%) as a light brown solid (from chloroform–hexane), m.p. 98—99 °C; δ_C (20 MHz; $CDCl_3$) 18.28 (q, SMe), 126.03, 127.4, 128.81, and 130.21 (arom C), 130.31 (C-4), 134.43 [s, C-3(5)], and 139.81 [s, C-5(3)] (Found: C, 58.2; H, 5.0; N, 20.7.

$C_{10}H_{11}N_3S$ requires C, 58.53; H, 5.36; N, 20.48%). The i.r. ^1H n.m.r., and mass spectral data are described in the text.

The other bromoketene dithioacetals (**2d—d**) and (**2e—g**) reacted similarly with hydrazine hydrate in refluxing ethanol, and work-up of the reaction mixture as described above afforded the corresponding pyrazoles (**7b—d**), (**8b, c**) (**9b—d**), and (**9e—g**).

3(5)-(p-*Chlorophenyl*)-4,5(3)-*bis*(*methylthio*)*pyrazole* (**7b**) (38%) was isolated as a white solid (from chloroform–hexane), m.p. 145—146 °C; $\nu_{max.}$(KBr) 3 185br, 1 602, 1 550, and 1 495 cm^{-1}; $\delta_H(CDCl_3)$ 2.17 (s, 3 H, SMe), 2.52 (s, 3 H, SMe), 7.25—8.01 (m, 4 H, ArH), 12.50 (br s, 1 H, NH, exchangeable with D_2O) (Found: C, 48.6; H, 3.9; N, 10.5. $C_{11}H_{11}ClN_2S_2$ requires C, 48.79; H, 4.06; N, 10.35%); *m/z* 270 (M^+).

3(5)-(*p*-Chlorophenyl)pyrazole (**8b**) (8%) was isolated as white solid (from hexane), m.p. 99 °C (lit.,[11] 98 °C); $\nu_{max.}$(KBr) 3 170, 1 598w, 1 505, and 1 442 cm^{-1}; $\delta_H(CDCl_3)$ 6.65 (br s, 1 H, 4-H) and 7.19—7.76 [m, 5 H, 5(3)-H + ArH] (Found: C, 60.8; H, 4.1; N, 15.5. Calc. for $C_9H_7ClN_2$: requires C, 60.50; H, 3.92; N, 15.68%).

4-*Amino*-3(5)-(p-*chlorophenyl*)-5(3)-*methylthiopyrazole* (**9b**) (31%) was isolated as light brown crystals (from chloroform–hexane), m.p. 150—151 °C; $\nu_{max.}$(KBr) 3 365, 3 130, 1 598, and 1 492 cm^{-1}; $\delta_H(CDCl_3)$ 2.40 (br s, 3 H, SMe), 5.22 (br s, 3 H, NH + NH_2, exchangeable with D_2O), and 7.28—7.87 (dd, 4 H, ArH) (Found: C, 49.9; H, 4.3; N, 17.3. $C_{10}H_{10}ClN_3S$ requires C, 50.10; H, 4.17; N, 17.53%); *m/z* 239, 241 (M^+).

4,5(3)-*Bis*(*methylthio*)-3(5)-(p-*tolyl*)*pyrazole* (**7c**) (41%) was isolated as a white solid (from chloroform–hexane), m.p. 135—136 °C; $\nu_{max.}$(KBr) 3 250br, 1 620, 1 566, and 1 502 cm^{-1}; $\delta_H(CDCl_3)$ 2.19 (s, 3 H, SMe), 2.42 (s, 3 H, SMe), 2.49 (s, 3 H, MeC_6H_4), 7.20—7.66 (dd, 4 H, ArH), and 12.0 (br s, 1 H, NH, exchangeable with D_2O) (Found: C, 57.8; H, 5.5; N, 12.1. $C_{12}H_{14}N_2S_2$ requires C, 57.60; H, 5.60; N, 11.92%); *m/z* 250 (M^+).

3(5)-(p-*Tolyl*)*pyrazole* (**8c**) (10%) was isolated as a white solid (from hexane), m.p. 76—77 °C; $\nu_{max.}$(KBr) 3 150, 1 508, and 1 458 cm^{-1}; $\delta_H(CDCl_3)$ 2.33 (s, 3 H, MeC_6H_4), 6.50 (br s, 1 H, 4-H), 6.90—7.70 (m, 5 H, 5-H + ArH), and 11.81 (br s, 1 H, NH, exchangeable with D_2O) (Found: 76.0; H, 6.2; N, 17.5. $C_{10}H_{10}N_2$ requires C, 75.90; H, 6.32; N, 17.72%).

4-*Amino*-5(3)-*methylthio*-3(5)-(p-*tolyl*)*pyrazole* (**9c**) (32%) was isolated as a light brown solid (from chloroform–hexane), m.p. 125—126 °C; $\nu_{max.}$(KBr) 3 330, 3 135, 1 585, and 1 506 cm^{-1}; $\delta_H(CDCl_3)$ 2.45 (s, 3 H, SMe); 5.62 (br s, 3 H, NH + NH_2, exchangeable with D_2O), and 7.32—7.64 (dd, 4 H, ArH) (Found: C, 60.5; H, 5.8; N, 19.4. $C_{11}H_{13}N_3S$ requires C, 60.27; H, 5.93; N, 19.17%); *m/z* 219 (M^+).

4,5(3)-*Bis*(*ethylthio*)-3(5)-*phenylpyrazole* (**7d**) (42%) was isolated as a viscous semisolid; $\nu_{max.}$($CHCl_3$) 3 148br, 1 593w, 1 563w, and 1 452s cm^{-1}; $\delta_H(CDCl_3)$ 0.96—1.5 (2 t, 6 H, 2 SCH_2Me), 2.69 (q, 2 H, SCH_2Me), 2.98 (q, 2 H, SCH_2Me), 7.20—7.48 (m, 3 H, ArH), 7.60—7.90 (m, 2 H ArH), and 10.9 (br, s, 1 H, NH, exchangeable with D_2O) (Found: C, 59.3; H, 5.9; N, 10.7. $C_{13}H_{16}N_2S_2$ requires C, 59.09; H, 6.06; N, 10.60%); *m/z* 264 (M^+).

4-*Amino*-5(3)-*ethylthio*-3(5)-*phenylpyrazole* (**9d**) (35%) was isolated as light brown crystals (from chloroform–hexane), m.p. 109—110 °C; $\nu_{max.}$(KBr) 3 318, 3 125, 1 582, and 1 460 cm^{-1}; $\delta_H(CDCl_3)$ 1.24 (t, 3 H, SCH_2Me), 2.72 (q, 2 H, SCH_2Me), 4.7 (br s, 3 H, NH + NH_2, exchangeable with D_2O), 7.2—7.5 (m, 3 H, ArH), and 7.60—7.75 (m, 2 H, ArH) (Found: C, 60.1; H, 6.2; N, 19.0. $C_{11}H_{13}N_3S$ requires, C, 60.27; H, 5.93; N, 19.17%); *m/z* 219 (M^+).

5,6-*Dihydro*-3-*phenyl*-1(2)H-[1,4]*dithiino*[2,3-c]*pyrazole* (**7e**) (76%) was isolated as needles (from ethanol), m.p. 141 °C; $\nu_{max.}$(KBr) 3 150, 3 065, 1 600br, and 1 491 cm^{-1}; $\delta_H(CDCl_3)$ (2.98—3.24 (2 t, 4 H, $S[CH_2]_2S$), 7.15—7.44 (m, 3 H, ArH), 7.5—7.69 (m, 2 H, ArH), and 10.85 (br s, 1 H, NH, exchangeable with D_2O) (Found: C, 56.3; H, 4.4; N, 12.2. $C_{11}H_{10}N_2S_2$ requires C, 56.41; H, 4.27; H, 11.96%); *m/z* 234 (M^+).

3-(p-*Chlorophenyl*)-5,6-*dihydro*-1(2)H-[1,4]*dithiino*[2,3-c]-*pyrazole* (**7f**) (80%) was isolated as needles (from ethanol), m.p. 166—167 °C; $\nu_{max.}$(KBr) 3 145, 3 075, 1 602br, and 1 493 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 3.09—3.37 (2 t, 4 H, $S[CH_2]_2S$), 7.32—7.62 (dd, 4 H, ArH), and 11.7 (br s, 1 H, NH, exchangeable with D_2O) (Found: C, 49.2; H, 3.4; N, 10.3. $C_{11}H_9ClN_2S_2$ requires C, 49.16; H, 3.35; N, 10.42%); *m/z* 268 (M^+).

5,6-*Dihydro*-3-(p-*methoxyphenyl*)-1(2)H-[1,4]*dithiino*[2,3-c]-*pyrazole* (**7g**) (62%) was isolated as needles (from ethanol), m.p. 143—144 °C $\nu_{max.}$(KBr) 3 102, 1 602, and 1 560 cm^{-1}; $\delta_H[(CD_3)_2]$ 3.04—3.3 (2t, 4 H, $S[CH_2]_2S$), 3.73 (s, 3 H, OMe), 6.85—7.51 (dd, 4 H, ArH), and 11.36 (br s, 1 H, NH, exchangeable with D_2O) (Found: C, 54.7; H, 4.4; N, 10.7. $C_{12}H_{12}N_2OS_2$ requires C, 54.54; H, 4.54; N, 10.60%); *m/z* 264 (M^+).

4-(*Benzylideneamino*)-5(3)-*methylthio*-3(5)-*phenylpyrazole* (**12**).—A solution of the amine (**9a**) (0.23 g, 2 mmol) and freshly distilled benzaldehyde (0.3 g, 2.5 mmol) was refluxed in dry ethanol (15 ml) for 30 h. The reaction mixture was then concentrated and the residue, on filtration through a small column of silica gel with chloroform as eluant, afforded the *title compound* (**12**) (0.2 g, 35%) as a light pink solid (from chloroform–hexane), m.p. 186—187 °C; $\nu_{max.}$(KBr) 3 152br and 1 610 cm^{-1}; $\delta_H(CDCl_3)$ 2.48 (s, 3 H, SMe), 7.22—7.87 (m, 10 H, Ph), and 8.69 (br, s, 1 H, N=CH) (Found: C, 70.1; H, 5.4; N, 14.6. $C_{17}H_{15}N_3S$ requires C, 69.92; H, 5.11; N, 14.33%); *m/z* 293 (M^+).

Alternative Synthesis of 4-*Amino*-5(3)-*methylthio*-3(5)-*phenylpyrazole* (**9a**).—(a) 5(3)-*Methylthio*-4-*nitroso*-3(5)-*phenylpyrazole* (**13**). To an ice-cooled (0—10 °C) solution of compound (**11**; Ar = Ph, R = Me) (1.9 g, 0.01 mmol) and pyridine (0.79 g, 0.01 mmol) in dry chloroform (70 ml) was added a solution of nitrosyl chloride (0.012 mmol) in ether (10 ml) in one lot; the solution immediately turned green. The reaction mixture was then stirred for 15 min, poured into water (100 ml), and extracted with chloroform (2 × 75 ml); the combined extracts were washed with water (100 ml), dried (Na_2SO_4), and evaporated to give a dark residue, which on crystallisation (chloroform–hexane) afforded the nitroso compound (**13**) (1.93 g, 88%) as dark green solid. A portion of compound (**13**) on recrystallisation from ethanol gave dark green needles, m.p. 187—188 °C; $\nu_{max.}$(KBr) 3 135 and 1 498 cm^{-1}; $\delta_H(CDCl_3)$ 2.33 (s, 3 H, SMe), 6.86—7.10 (m, 3 H, ArH), and 7.35—7.56 (m, 2 H, ArH) (Found: C, 54.7; H, 4.2; N, 19.1. $C_{10}H_9N_3OS$ requires C, 54.79; H, 4.10; N, 19.17%).

(b) *Reduction of compound* (**13**) Zinc dust (2 g) was added to a solution of compound (**13**) (1.1 g, 5 mmol) and glacial acetic acid (1 ml) in ethanol (30 ml), and the mixture was refluxed for 1 h. The cooled solution was then poured into water (100 ml) and extracted with chloroform (2 × 75 ml); the extract was washed with water (50 ml), dried (Na_2SO_4), and evaporated to give a viscous residue, which on column chromatography over silica gel with chloroform as eluant furnished the amine (**9a**) as light brown crystals, m.p. 98—99 °C, identical with the sample prepared previously (mixed m.p., superposable i.r. and n.m.r. spectra).

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