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BRIDGEHEAD NITROGEN HETEROCYCLES FROM 2,4,6-TRIPHENYL-PYRYLIUM CATION AND THIOSEMICARBAZIDE OR THIOCARBOHYDRAZIDE

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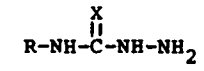
Abstract: 2,4,6-Triphenylpyrylium with thiosemicarbazide and thiocarbohydrazide, gives 2-pyrazolines 3a and 3b which undergo cyclization yielding pyrazolo[1,5-c]pyrimidine 5 and pyrazolo[2,3-d]-1,2,4-triazepine 7 derivatives, respectively. Reaction of 7 with phenacyl bromides gave 1,3-thiazolo[3,2-b]pyrazolo[2,3-d]-1,2,4-triazepin-4-iums 10. Compound 3a on treatment with phenacyl bromides gave 1-(4'-aryl-thiazol-2'-yl)-2-pyrazoline derivatives 6. Compound 3b reacts with acyl chlorides to give pyrazolo[1,5-c]pyrimidine derivatives 14, and with aromatic aldehydes giving the 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-Δ^{2}-thiadiazolines 12 which were easily converted to the corresponding 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-thiadiazoles 13.

The reaction of pyrylium salts with 1,2-bifunctional nitrogen nucleophiles may afford, according to reaction conditions and substitution pattern of the reactants, five-membered or seven-membered nitrogen heterocycles.

The reaction of 1,2-bifunctional nitrogen heterocycles with several pyrylium salts to give five-membered or seven-membered nitrogen heterocycles, has been comprehensively reviewed[1]; however, reactions of pyrylium salts with compounds type 1 have not received very much attention; it has only briefly mentioned that 2,4,6-triphenylpyrylium tetrafluoroborate reacts with semicarbazide in ethanolic solution to form the ureido derivative[2]. However, when the reaction is carried out in dimethylformamide in the presence of potassium acetate, 7-oxo-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine is formed[3].

On the other hand, we have reported[4] the reaction of 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate with thiocarbohydrazide to give 3-amino-4-oxo-6,8-diphenyl-3,4-dihydropyrido[2,1-f]-1,2,4-triazin-9-ium-2-thiolate.



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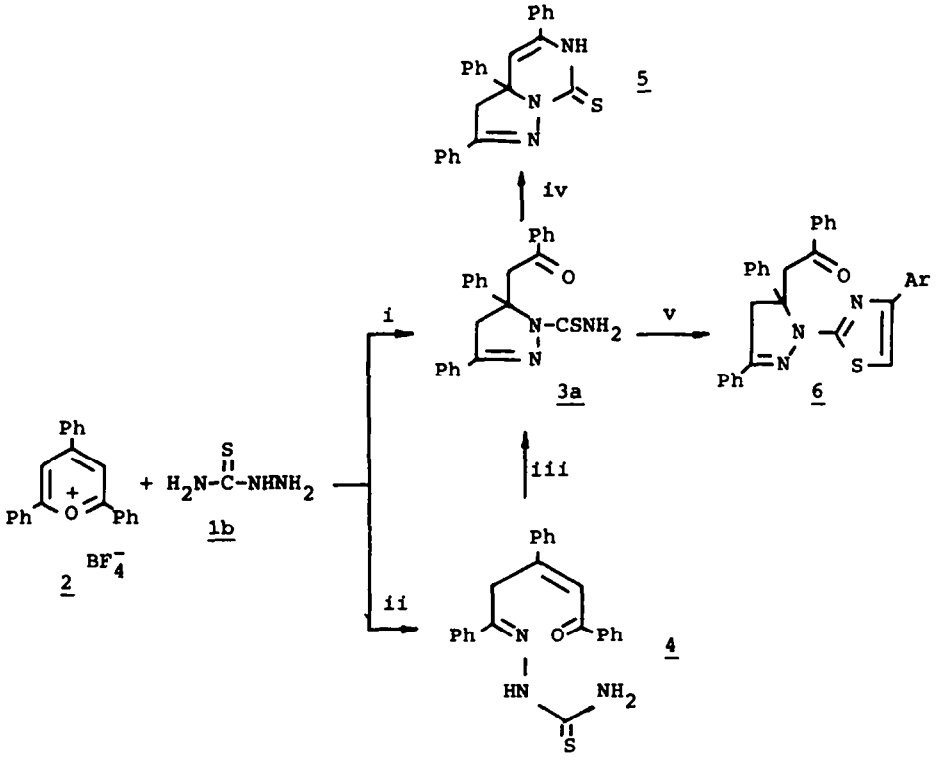
a: R = H X = O
b: R = H X = S
c: R = NH_2 X = S

Reaction of 2,4,6-Triphenylpyrylium Salts with Thiosemicarbazide

The pyrylium salt 2 reacts with thiosemicarbazide 1b at reflux temperature in ethanol in the presence of triethylamine to give the monocyclic compound 3a as crystalline solid, in 78% yield. The i.r. spectrum of 3a shows absorptions in the region 3500-3383 cm^{-1} due to the amino group and at 1695 cm^{-1} which can be attributed to the carbonyl stretching vibration. The ^{1}H-n.m.r. spectrum shows two double doublets near 3.9 and 4.9 ppm (J=18 Hz), respectively, indicating two methylene groups with non-equivalent protons. The mass spectrum shows the expected molecular ion and peaks are also shown for the loss of H_2O and Ph-CO-CH_3 from the molecular ion; the base peak occurs at m/z 77.

Compound 2 reacts with thiosemicarbazide at room temperature in ethanol in the presence of triethylamine to give the monothiosemicarbazone 4, as crystalline solid in 70% yield. Support for the formula 4 is clearly provided by the i.r. spectrum which shows a strong band at 1666 cm^{-1} corresponding to the N-H stretching vibration. In the ^{1}H-n.m.r. spectrum appears among others a singlet at δ 3.8 ppm indicating a -CH_2- group and a singlet at δ 6.15 ppm indicating a =CH- group. When compound 4 is heated in ethanolic solution undergoes cyclization to the monocyclic compound 3a in almost quantitative yield.

The pyrazoline 3a on treatment with acetic acid in boiling ethanol cyclised to the bicyclic compound 5 in 85% yield. Structure 5 is based on spectral evidence. The ^{1}H-n.m.r. spectrum shows the -CH_2-group as a singlet at δ 4.0 ppm, the =CH- singlet at δ 6.3 ppm, and the NH singlet at δ 9.9 ppm, in addition to the aromatic protons. The mass spectrum shows the expected molecular ion, and the base peak occurs at M^+-77 for the loss of C_6H_5.



i: Et_3N/EtOH/Δ ; ii: Et_3N/EtOH/R.T. ; iii: Δ ; iv: EtOH/AcOH/Δ ;
v: Ar-$COCH_2$Br/MeOH/Δ .

The pyrazoline 3a reacts with phenacyl bromides in boiling methanol to give the 1-(thiazol-2'-yl)-2-pyrazolines 6 as crystalline solids in good yields. Similar results were achieved by reaction of the bicyclic compound 5 with phenacyl bromides. Structures 6 are based on microanalytical data and spectral evidence. The i.r. spectra show a strong absorption at 1678-1684 cm^{-1} due to the carbonyl group. The ^{1}H-n.m.r. spectra show as characteristic signals a singlet at δ 4.6 ppm attributable to the endocyclic methylene group and a double doublet at δ 3.3-4.3 ppm (J=18 Hz) corresponding to the exocyclic methylene group. Mass spectra show the expected molecular ion peak for 6; the base peak generally occurs at m/z 77 and the m/z 105 fragment is present in all the cases (62-100%).

Reaction of 2,4,6-Triphenylpyrylium Salt with Thiocarbohydrazide.

Compound 2 reacts with thiocarbohydrazide 1c at room temperature in ethanol, in the presence of triethylamine to give the pyrazoline 3b as a crystalline solid in 85% yield. Support for the formulation 3b is clearly provided by spectral evidence. The i.r. spectrum shows a clear absorption at 1680 cm^{-1} which is assigned to the carbonyl stretching vibration; the presence of the primary and secondary amino groups is confirmed by the presence of bands in the region 3360-3200 cm^{-1}. Particularly significant in the ^{1}H-n.m.r. spectrum are the two AB quartets at δ 3.65-4.15 and δ 4.4-5.2 ppm respectively, for the methylene groups. The mass spectrum shows the molecular ion peak at m/z 414 and the base peak appears at m/z 105.

Compound 3b in boiling ethanol, in the presence of acetic acid, cyclises to the pyrazolo[2,3-d]-1,2,4-triazepin-8-thione 7, which undergoes S-methylation on reaction with methyl trifluoromethanesulfonate, in boiling dry dichloromethane, to give 8-methylthio-2,3a,5-triphenyl-3,3a,4,7-tetrahydropyrazolo[2,3-d]-1,2,4-triazepin-7-ium trifluoromethanesulfonate 8 as crystalline solid in 86% yield. Compound 8 is also obtained when the monocyclic compound 3b is treated with methyl trifluoromethanesulfonate under the conditions described previously.

The structural elucidation of compounds 7 and 8 was accomplished on the basis of spectral and microanalytical data. The i.r. spectra of compounds 7 and 8 show absorption at 3180 cm^{-1} attributable to the NH stretching vibration, while their ^{1}H-n.m.r. spectra present as characteristic signals a multiplet at δ 3.6-4.9 ppm due to the two methylene groups; the ^{1}H-n.m.r. spectrum of compound 8 also presents a singlet at δ 2.85 ppm attributable to the S-methyl group. The mass spectrum of 7 shows the expected molecular ion peak at m/z 396 while the fragment at $M^+-CF_3SO_3$ is the molecular ion peak in the mass spectra of 8, which also shows the fragment at m/z 363 ($M^+-CF_3SO_3-CH_3SH$).

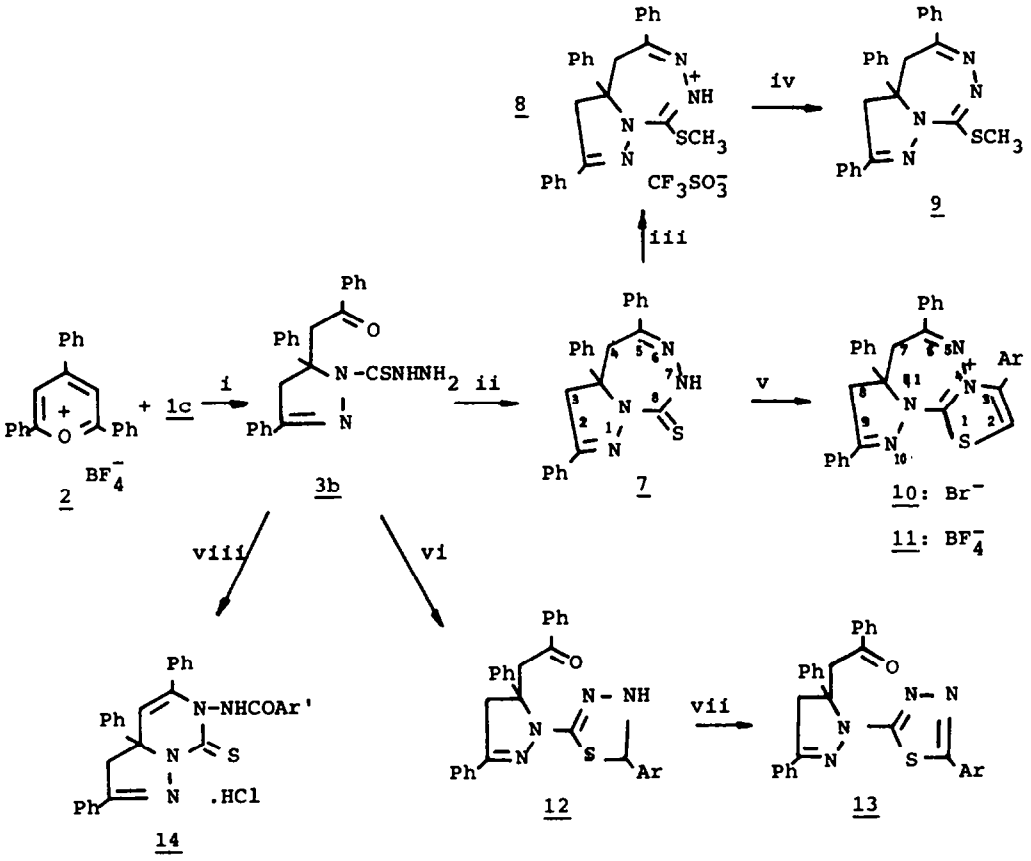
When compound 8 is treated with triethylamine or potassium hydroxide in methanolic solution at reflux temperature for 2 h. the 8-methylthio-2,3a,5-triphenyl-3a,4-dihydro-3H-pyrazolo[2,3-d]-1,2,4-triazepine 9 is obtained in moderate yield.

On the other hand, the cyclocondensation of α-halocarbonyl compounds with 7 gives the tricyclic system 1,3-thiazolo[3,2-b]pyrazolo[2,3-d]-1,2,4-triazepin-4-ium 10 in high yields (76-87%). Structural elucidation of 10 was accomplished on the basis of spectral data and microanalysis. In particular, each compound displayed in the ^{1}H-n.m.r. spectra a multiplet at δ 3.7-5.2 ppm due to the two methylene groups present in the system. In the mass spectra the expected molecular ion peak does not appear. Compounds 10, are converted in almost quantitative yields into the corresponding tetrafluoroborates 11 by treatment with tetrafluoroboric acid. The preparation of compounds 10 appears to be quite general and it proceeds satisfactorily both when the aromatic ring is substituted by electron-

donating and withdrawing groups.

Compound 3b reacts with aromatic aldehydes at reflux temperature in ethanol giving the corresponding 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-Δ^{2}-thiadiazolines 12, which on treatment with chloranil at reflux temperature in benzene, undergo oxidation to yield the corresponding 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-thiadiazoles 13.

Support for structure 12 is based on microanalytical data and spectral evidence. The i.r. spectra of 12 and 13 show a strong band at 1684 cm^{-1} due to the carbonyl group; in addition, compounds 12 also show at 3300 cm^{-1} the characteristic absorption band of the NH group. The ^{1}H-n.m.r. spectra of 12 show two double doublets at δ 3.55-4.15 and δ 4.25-5.75 ppm (J=18 Hz) due to the non-equivalent protons of the two methylene groups; the signal corresponding to the 5-H is included into the aromatic multiplet, which is in good agreement with the literature data[5,6]. Mass spectra of 12 show the expected molecular ion peak and fragments at M^{+}-1 and M^{+}-2 are also found. The ^{1}H-n.m.r. spectra of 13 show a singlet at δ 4.75 ppm due to the endocyclic methylene group and a double doublet at δ 3.35-4.50 (J=18 Hz), attributable to the exocyclic methylene group; mass spectra show the molecular ion peak and the base peak occurs at m/z 105.



i: Et_3N/EtOH/Δ ; ii: EtOH/AcOH/ Δ ; iii: CF_3SO_3Me; iv: Et_3N/MeOH; v: Ar-CO-CH_2Br; vi: Ar-CHO/EtOH/Δ ; vii: chloranil/C_6H_6/Δ ; viii: Ar'-COCl/C_6H_6/Δ .

On the other hand, reaction of 3b with aroyl chlorides at reflux temperature in dry benzene gives the corresponding pyrazolo[1,5-c]pyrimidine 14. Structural elucidation of 14 was accomplished on the basis of microanalysis and spectral evidence. The i.r. spectra show a strong absorption at 1693 cm^{-1} which is assigned to the carbonyl stretching vibration; the presence of the amino group is confirmed by the absorption band at 3300 cm^{-1}. The ^{1}H-n.m.r. spectra show as characteristic signals two singlets at δ 3.65 ppm and δ 5.9 ppm respectively, attributables to the methylene and =CH- groups. Mass spectra show the molecular ion peak at M^+-Cl, and the fragment Ar'-CO^+ is the base peak.

EXPERIMENTAL

All melting points were determined using a Kofler hot-stage microscope and are uncorrected. I.R. spectra were recorded with a Nicolet Ft 5DX spectrometer. ^{1}H-n.m.r. spectra were recorded at 60 MHz on a Varian EM-360A spectrometer using tetramethyl silane as internal standard; in some cases, drops of TFA were added to improve the solubility of the samples which were insolubles in the common solvents. Mass spectra (70 eV) were obtained using a Hewlett Packard 5993C instrument. Combustion analyses were performed with a Perkin-Elmer 240-C instrument.

1-Aminothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline. 3a. To a well stirred solution of 2,4,6-triphenylpyrylium tetrafluoroborate 2 (1 g., 2.5 mmol) and triethylamine (0.252 g., 2.5 mmol) in ethanol (30 ml), thiosemicarbazide 1b (0.23 g., 2.5 mmol) was added. The reaction mixture was heated under reflux temperature for 3 h. and on cooling the 2-pyrazoline (0.8 g., 78%) was separated as prisms; m.p. 191-193°C from EtOH. (Found: C, 71.98; H, 5.13; N, 10.40; $C_{24}H_{21}N_3OS$ requires C, 72.18; H, 5.26; N, 10.52%); I.R. (nujol): 3500, 3383, 1695, 1568, 1525, 1493, 1462, 1446, 1363, 1340, 1242, 1205, 1091, 1066, 856, 758 and 688 cm^{-1}. δ ($CDCl_3$/TFA): 3.7 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 5.5 (d, 1H, J=18 Hz), 6.7 (s, 2H), 7.4-8.2 (m, 15H); m/z (%): 399 (38), 381 (25), 304 (75), 281 (13), 280 (53), 279 (45), 221 (77), 220 (59), 219 (12), 176 (14), 118 (8), 105 (92), 104 (24), 103 (22), 77 (100).

5-Oxo-1,3,5-triphenylpent-3-ene-1-Thiosemicarbazone. 4. 2,4,6-Triphenylpyrylium tetrafluoroborate 2 (1 g., 2.5 mmol), ethanol (30 ml), triethylamine (0.25 g., 2.5 mmol) and thiosemicarbazide (0.23 g., 2.5 mmol), were stirred at room temperature for 4 h. The thiosemicarbazone (0.71 g, 70%) separated as prisms; m.p. 142-143°C from EtOH. (Found: C, 72.03; H, 5.21; N, 10.36. $C_{24}H_{21}N_3OS$ requires C, 72.18; H, 5.26; N, 10.52%). IR (Nujol): 3420, 3296, 3273, 3143, 1666, 1585, 1477, 1444, 1223, 1074, 1000, 874, 777, 763, 756, 750 and 690 cm^{-1}. δ ($CDCl_3$/TFA) 3.8 (s, 2H), 6.15 (s, 1H), 7.2 (s, 2H), 7.4-8.1 (m, 15H), 8.6 (s, 1H). m/z (%): 399 (42), 381 (15), 191 (24), 105 (97), 104 (23), 103 (23), 77 (100).

2,3a,5-Triphenylpyrazolo[1,5-c]pyrimidin-7-thione. 5. 1-Aminothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3a (0.8 g., 2.1 mmol) was suspended in ethanol (30 ml) and acetic acid (3 ml) was added. The reaction mixture was stirred at reflux temperature for 12 h. and the precipitated solid was filtered off and recrystallised from ethanol (0.53 g, 85%); m.p. 260-263°C. (Found: C, 75.40; H, 4.77; N, 10.81; $C_{24}H_{19}N_3S$ requires C, 75.59; H, 4.98; N, 11.02%). IR (Nujol): 3325, 1643, 1525, 1495, 1452, 1437, 1379, 1278, 1246, 1093, 950, 873, 833, 758, 742 and 690 cm^{-1}; δ ($CDCl_3$/TFA): 4.0 (s, 2H), 6.3 (s, 1H), 7.3-8.1 (m, 15H), 9.9 (s, 1H); m/z (%): 381 (33), 304 (100), 245 (12), 104 (6), 103 (5), 77 (16).

General Procedure for the Preparation of 1-(4'-aryl-thiazol-2'-yl)-5-phenacyl-2,5-diphenyl-2-pyrazolines. 6. 1-Aminothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3a (0.399 g, 1 mmol), in dry methanol (20 ml) and an equimolecular amount of the corresponding phenacyl bromide, were refluxed for 12 h. The resulting precipitates were recrystallised from $CHCl_3$/EtOH (1:1). The following derivatives were obtained: 1-(4'-phenyl-thiazol-2'-yl)- (81%), prisms, m.p. 155-157°C. (Found: C, 76.71; H, 4.87; N, 8.39; $C_{32}H_{25}N_3OS$ requires C, 76.95; H, 5.01; N, 8.41%). IR (Nujol): 1687, 1599, 1545, 1520, 1496, 1446, 1383, 1359, 1340, 1329, 1203, 1180, 1159, 1072, 1053, 987, 922, 885, 760, 719 and 692 cm^{-1}; δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.6 (s, 2H), 6.6 (s, 1H), 6.9-8.3 (m, 20H); m/z (%): 499 (7), 380 (14), 379 (5), 219 (2), 191 (2), 134 (20), 129 (16), 121 (3), 120 (5), 117 (7), 115 (19), 105 (62), 104 (10), 103 (13), 77 (100).

1-(4'-p-methoxyphenyl-thiazol-2'-yl)- (87%), prisms, m.p. 202-204°C. (Found: C, 74.68; H, 4.90; N, 7.70; $C_{32}H_{27}N_3O_2S$ requires C, 74.85; H, 5.10; N, 7.93%). IR (Nujol): 1689, 1545, 1487, 1466, 1446, 1359, 1321, 1286, 1248, 1203, 1147, 1161, 1053, 842, 756, 738, 690 and 673 cm^{-1}; δ ($CDCl_3$): 3.7 (s, 3H), 3.8 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.65 (s, 2H), 6.6 (s, 1H), 6.8-8.2 (m, 19H); m/z (%): 529 (25), 410 (61), 409 (29), 309 (10), 307 (15), 219 (5), 206 (10), 191 (7), 189 (11), 159 (18), 133 (7), 121 (12), 120 (8), 117 (15), 105 (83), 77 (100). 1-(4'-p-chlorophenyl-thiazol-2'-yl)- (73%), prisms, m.p. 209-210°C. (Found: C, 71.82; H, 4.30; N, 7.59; $C_{32}H_{24}ClN_3OS$ requires C, 71.97; H, 4.49; N, 7.87%). IR (Nujol): 1676, 1539, 1494, 1475, 1446, 1358, 1327, 1319, 1205, 1155, 1087, 1051, 1010, 991, 920, 841, 794, 754, 733, 692 and 667 cm^{-1}; δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.6 (s, 2H), 6.7 (s, 1H), 7.0-8.3 (m, 19H); m/z (%): 535 (7), 533 (17), 416 (12), 414 (29), 415 (12), 413 (12), 219 (4), 165 (5), 163 (9), 138 (4), 136 (7), 117 (9), 115 (24), 105 (81), 104 (11), 103 (15), 77 (100). 1-(4'-p-bromophenyl-thiazol-2'-yl)- (74%), prisms, m.p. 212-215°C. (Found: C, 66.18; H, 4.06; N, 7.11; $C_{32}H_{24}BrN_3OS$ requires C, 66.43; H, 4.15; N, 7.26%). IR (Nujol): 1678, 1537, 1516, 1494, 1466, 1446, 1396, 1377, 1358, 1317, 1205, 1155, 1049, 1006, 837, 794, 754, 731 and 690 cm^{-1}. δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.65 (s, 2H), 6.6 (s, 1H), 6.9-8.3 (m, 19H); m/z (%): 579 (5), 577 (5), 460 (32), 458 (36), 459 (37), 457 (28), 220 (4), 219 (4), 209 (4), 207 (6), 191 (4), 182 (5), 180 (5), 157 (3), 155 (3), 121 (14), 120 (17), 119 (8), 117 (18), 115 (28), 105 (97), 104 (11), 103 (16), 77 (100). 1-(4'-p-nitrophenyl-thiazol-2'-yl)- (68%),plates, m.p. 231-234°C. (Found: C, 70.37; H, 4.20; N, 10.12; $C_{32}H_{24}N_4O_3S$ requires C, 70.58; H, 4.41; N, 10.29%). IR (Nujol): 1693, 1597, 1545, 1496, 1464, 1446, 1377, 1344, 1317, 1205, 1180, 1109, 1053, 854, 821, 785, 769, 750, 721, 702 and 684 cm^{-1}.δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.6 (s, 2H), 6.6 (s, 1H), 6.7-8.4 (m, 19H); m/z (%): 544 (8), 425 (49), 424 (18), 219 (8), 174 (6), 120 (17), 119 (8), 117 (11), 115 (25), 105 (89), 77 (100). 1-(4'-p-biphenylyl-thiazol-2'-yl)- (81%), prisms, m.p. 206-208°C (Found: C, 79.15; H, 4.90; N, 7.23; $C_{38}H_{29}N_3OS$ requires C, 79.30; H, 5.04; N, 7.30%). IR (Nujol): 1684, 1597, 1547, 1529, 1479 1466, 1446, 1379, 1369, 1327, 1257, 1207, 1153, 1055, 1003, 995, 844, 790, 767, 754, 736, 700 and 692 cm^{-1}. δ ($CDCl_3$) 3.75 (d, 1H, J=18 Hz), 4.3 (d, 1H, J=18 Hz), 4.6 (s, 2H), 6.6 (s, 1H), 7.0-8.4 (m, 24H); m/z (%): 575 (8), 456 (43), 455 (45), 454 (9), 422 (26), 219 (3), 210 (22), 205 (6), 178 (23), 165 (19), 152 (14), 120 (19), 119 (4), 117 (9), 115 (19), 105 (88), 77 (100).

1-Hydrazinothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline. 3b. Thiocarbohydrazide (0.12 g, 1.25 mmol) was added to a stirred solution of 2,4,6-triphenylpyrylium tetrafluoroborate (0.5 g, 1.25 mmol) and triethylamine (0.127 g, 1.25 mmol), in ethanol (30 ml). The solution was stirred at room temperature for 6 h. and the 2-pyrazoline which separated on cooling was recrystallised from EtOH/$CHCl_3$ (1:1). (0.44 g, 85%); m.p. 183-184°C. (Found: C, 69.30; H, 5.27; N, 13.32; $C_{24}H_{22}N_4OS$ requires C. 69.56; H, 5.31; N, 13.52%). IR (Nujol): 3360, 3290, 3200, 1680, 1600, 1480, 1450, 1400, 1360, 1320, 1310, 1260, 1240, 1210, 1070, 1055, 1010, 1005, 995, 985, 910, 790, 770, 710, 695 and 670 cm^{-1}. δ ($CDCl_3$/TFA): 3.65 (d, 1H, J=18 Hz), 4.15 (d, 1H, J=18 Hz), 4.4 (d, 1H, J=18 Hz), 5.25 (d, 1H, J=18 Hz), 6.8 (s, 2H), 7.3-8.9 (m, 16H); m/z (%): 414 (8), 309 (20), 222 (15), 221 (90), 220 (57), 193 (12), 191 (15), 189 (9), 115 (12), 105 (100), 104 (22), 103 (15), 91 (16), 77 (87).

3,3a,4,7-Tetrahydro-2,3a,5-triphenylpyrazolo[2,3-d]-1,2,4-triazepin-8-thione. 7. To a solution of 1-hydrazinothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3b (0.3 g, 0.724 mmol) in ethanol (20 ml), acetic acid (2 ml) was added. The reaction mixture was heated at reflux temperature for 16 h. and the precipitated solid was filtered off and recrystallised from ethanol. (0.25 g, 89%); m.p. 284-285°C. (Found: C, 72.68, H, 4.95; N, 14.06; $C_{24}H_{20}N_4S$ requires C, 72.72; H, 5.05, N, 14.14%). IR (Nujol): 3180, 1460, 1455, 1380, 1360, 1290, 1245, 770, 765, 760, 710, 700 and 690 cm^{-1}. δ ($CDCl_3$/TFA): 3.75-4.9 (m, 4H), 7.3-8.6 (m, 16H); m/z (%): 396 (18), 292 (11), 279 (5), 222(16), 221 (100), 220 (27), 219 (9), 191 (13), 190 (15), 189 (12), 176 (6), 147 (12), 117 (19), 115 (15), 104 (30), 103 (46), 91 (25), 77 (65).

3,3a,4,7-Tetrahydro-8-methylthio-2,3a,5-triphenylpyrazolo[2,3-d]1,2,4-triazepin-7-ium Trifluoromethanesulfonate. 8. Method A: To a stirred solution of 3,3a,4,7-tetrahydro-2,3a,5-triphenylpyrazolo[2,3-d]1,2,4—triazepin-8-thione 7 (0.2 g., 0.5 mmol), in dry methylene chloride (20 ml), methyl trifluoromethanesulfonate (0.082 g, 5 mmol) was added dropwise. After 2 h. at reflux temperature, the solvent was removed under reduced pressure. Et_2O (10 ml) precipitated the pyrazolo [2,3-d]1,2,4-triazepin-7-ium (o.24 g, 86%); prisms, m.p. 224-226°C from ethanol. (Found: C, 55.53; H, 3.90; N, 9.87; $C_{26}H_{23}F_3N_4O_3S_2$ requires C, 55, 71; H, 4.10; N, 10.00%). IR (Nujol): 3200, 1637, 1599, 1572, 1562, 1521, 1498, 1466, 1446, 1375, 1347, 1305, 1277, 1250, 1226, 1170, 1157, 1032, 837, 765, 725, 700, 688 and 638 cm^{-1}.δ ($CDCl_3$/TFA): 2.85 (s, 3H), 3.6-4.8 (m, 4H), 6.9-7.9 (m, 15H); m/z (%): 411 (M^+-CF_3SO_3, 1), 395 (1), 363 (2), 279 (1), 278 (3), 221 (21), 220

(100), 219 (6), 191 (29), 189 (13), 165 (10), 119 (10), 118 (59), 117 (14), 104 (21), 103 (13), 91 (12), 77 (100).
Method B: As for method A, except that starting material was 1-hydrazinothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3b. The trifluoromethanesulfonate 8 was obtained in 82% yield.

3a,4-Dihydro-8-methylthio-2,3a,5-triphenyl-3H-pyrazolo[2,3-d]1,2,4-triazepine. 9. Method A: A solution of 3,3a,4,7-tetrahydro-8-methylthio-2,3a,5-triphenylpyrazolo 2,3-d 1,2,4-triazepin-7-ium trifluoromethanesulfonate (0.6 g, 1 mmol) and triethylamine (0.1 g, 1 mmol) in dry methanol (20 ml) was heated at reflux temperature for 2 h. On cooling the pyrazolo[2,3-d]1,2,4-triazepine precipitated (0.22 g, 50%). Prisms from EtOH, m.p. 208-210°C. (Found: C, 72.91; H, 5.27; N, 13.41; $C_{25}H_{22}N_4S$ requires C, 73.17; H, 5.36; N, 13.65%). IR (Nujol): 1510, 1493, 1466, 1448, 1373, 1040, 1275, 1240, 1087, 1066, 1033, 927, 914, 815, 769, 758, 704 and 692 cm^{-1}. δ ($CDCl_3$): 2.5 (s, 3H), 3.2-4.0 (m, 4H), 7.0-7.9 (m, 15H). m/z (%): 410 (9), 363 (3), 233 (15), 221 (21), 220 (40), 219 (8), 191 (15), 190 (15), 189 (9), 118 (15), 117 (98), 116 (11), 115 (25), 104 (25), 103 (84), 91 (21), 89 (10), 77 (100).
Method B: As for method A except that KOH (0.056 g, 1 mmol) was used instead of Et_3N. The product was obtained in 48% yield.

General Procedure for the Preparation of 3-Aryl-7a,8-dihydro-6,7a,9-triphenyl-7H-1,3-thiazolo[3,2-b]pyrazolo[2,3-d]1,2,4-triazepin-4-ium bromides. 10. 3,3a,4,7-Tetrahydro-2,3a,5-triphenylpyrazolo 2,3-d 1,2,4-triazepin-8-thione 7 (0.396 g, 1 mmol) in dry methanol (20 ml) and an equimolecular amount of the corresponding phenacyl bromide were stirred at reflux temperature for 6 h. On cooling, the precipitates formed were filtered off and recrystallised from methanol. 3,6,7a,9-Tetraphenyl- (83%), m.p. 243-245°C (prisms). (Found: C, 66.31; H, 4.28; N, 9.56; $C_{32}H_{25}BrN_4S$ requires C, 66.55; H, 4.33; N, 9.70%). IR (Nujol): 1604, 1587, 1575, 1496, 1450, 1377, 1348, 1330, 1190, 779, 765, 702 and 686 cm^{-1}. δ ($CDCl_3$/TFA): 3.65-4.9 (m, 4H), 7.0-8.0 (m, 21 H); m/z (%): 396 (3), 379 (1), 277 (1), 276 (3), 221 (26), 220 (100), 219 (7), 191 (24), 143 (4), 117 (14), 115 (8), 104 (19), 103 (9), 102 (10), 77 (78); 3-p-methoxyphenyl- (87%), m.p. 250-252°C (prisms). (Found: C, 65.18; H, 4.21; N, 9.17; $C_{33}H_{27}BrN_4OS$ requires C, 65.23; H, 4.44; N, 9.22%). IR (Nujol): 1608, 1579, 1508, 1464, 1450, 1377, 1344, 1302, 1259, 1182, 835, 769, 702 and 690 cm^{-1}. δ ($CDCl_3$/TFA): 3.9 (s, 3H), 4.o-5.2 (m, 4H), 7.0-8.2 (m, 20H); m/z (%): 409 (7), 396 (2), 307 (9), 306 (39), 221 (17), 220 (100), 219 (6), 191 (25), 143 (4), 132 (56), 117 (18), 115 (7), 107 (3), 104 (14), 103 (5), 77 (38); 3-p-bromophenyl- (70%), m.p. 191-192°C (prisms). (Found: C, 58.29; H, 3.51; N, 8.36; $C_{32}H_{24}Br_2N_4S$ requires C, 58.53; H, 3.65; N, 8.53%). IR (Nujol): 1609, 1591, 1577, 1466, 1450 1377, 1344, 1072, 1053, 829, 765 and 690 cm^{-1}. δ ($CDCl_3$/TFA): 4.0-5.1 (m, 4H) 7.1-8.0 (m, 20H); m/z (%): 459 (1), 457 (1), 396 (3), 356 (10), 355 (3), 354 (10), 353 (3), 221 (19), 220 (100), 219 (7), 191 (23), 182 (11), 180 (12), 157 (4), 155 (4), 143 (3), 117 (9), 115 (5), 104 (12), 103 (5), 77 (22). 3-p-chlorophenyl- (73%), m.p. 213-215°C, (prisms). (Found: C, 62.53; H, 3.70; N, 8.93; $C_{32}H_{24}BrClN_4S$ requires C, 62.79; H, 3.92; N, 9.15%). IR (Nujol): 1603, 1587, 1575, 1496, 1466, 1450, 1379, 1342, 1091, 1049, 1014, 831, 771, 761, 700 and 688 cm^{-1}. δ ($CDCl_3$/TFA): 4.1-5.2 (m, 4H), 7.2-8.3 (m, 20H); 3-p-nitrophenyl- (78%) m.p. 192-194°C (prisms) (Found: C, 61.56; H, 3.61; N, 10.97; $C_{32}H_{24}BrN_5O_2S$ requires C, 61.73; H, 3.85; N, 11.25%). IR (Nujol): 1610, 1590, 1580, 1520, 1460, 1450, 1380, 1350, 855, 840, 775, 760, 740 and 690 cm^{-1}. δ ($CDCl_3$/TFA): 3.6-5.0 (m, 4H), 7.1-8.3 (m, 20H); m/z (%): 424 (2), 396 (5), 322 (1), 321 (4), 221 (22), 220 (100), 219 (7), 191 (22), 147 (4), 143 (3), 122 (3), 117 (12), 115 (5), 104 (28), 103 (8), 77 (41); 3-p-biphenylyl- (70%), m.p. 234-237 °C (prisms). (Found: C, 69.71; H, 4.30; N, 8.42; $C_{38}H_{29}BrN_4S$ requires C, 69.83; H, 4.44; N, 8.57%). IR (Nujol): 1608, 1590, 1580, 1560, 1460, 1450, 1380, 1340, 840, 770, 760, 700 and 690 cm^{-1}. δ ($CDCl_3$/TFA): 3.7-5.1 (m, 4H), 7.1-8.5 (m, 25 H).

General Procedure for the Preparation of 3-Aryl-7a,8-dihydro-6,7a,9-triphenyl-7H-1,3-thiazolo[3,2-b]pyrazolo[2,3-d]1,2,4-triazepin-4-ium Tetrafluoroborates 11. To a solution of the 3-aryl-7a,8-dihydro-6,7a,9-triphenyl-7H-1,3-thiazolo 3,2-b pyrazolo 2,3-d 1,2,4-triazepin-4-ium bromides 10 (1 mmol) in ethanol (15 ml) tetrafluoroboric acid (1 ml) was added. The solution was heated under reflux temperature for 4 h. On cooling the corresponding tetrafluoroborates precipitated which were recrystallised from methanol. The spectroscopy characteristics of these salts were identical to the corresponding bromides except the absorption at 1060 cm^{-1} in the IR (BF_4^-). 3,6,7a,9-Tetraphenyl- (80%), m.p. 230°C (prisms). (Found: C, 65.70; H, 4.17; N, 9.39; $C_{32}H_{25}BF_4N_4S$ requires C, 65.75; H, 4.28; N, 9.58%); 3-p-methoxyphenyl- (83%), m.p. 228°C (prisms). (Found: C, 64.30, H, 4.12; N, 8.90; $C_{33}H_{27}BF_4N_4OS$ requires C, 64.49; H, 4.39; N, 9.12%).

General Procedure for the Preparation of 2-($\Delta^{2'}$-pyrazolin-1-yl)5-aryl-1,3,4-Δ^2-thiadiazolines. 12. 1-Hydrazinothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3b (0.414 g, 1 mmol) in EtOH (20 ml) and an equimolecular amount of aromatic aldehydes were refluxed for 16 h. The resulting products were filtered off and recrystallised from CH_2Cl_2/EtOH (2:1). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-phenyl- (82%), m.p. 182-182°C (prisms) (Found:C, 73.92; H, 5.20; N, 10.88; $C_{31}H_{26}N_4OS$ requires C, 74.10; H, 5.17; N, 11.15%). IR (Nujol): 3296, 1674, 1595, 1575, 1512, 1489, 1464, 1448, 1412, 1371, 1334, 1304, 1209, 1152, 952, 925, 895, 792, 752 and 684 cm^{-1}. δ ($CDCl_3$): 3.55 (d, 1H, J=18 Hz), 4.15 (d, 1H, J=18 Hz), 4.25 (d, 1H, J=18 Hz), 5.75 (d, 1H, J=18 Hz), 7.0-8.4 (m, 21 H); m/z (%): 502 (2), 501 (1), 500 (4), 383 (9), 382 (10), 381 (16), 380 (12), 307 (9), 246 (16), 221 (41), 220 (49), 191 (11), 120 (21), 119 (4), 105 (71), 104 (40), 103 (58), 77 (100). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-tolyl- (78%), m.p. 184-185°C (prisms) (Found: C, 74.21 H, 5.17; N, 10.63; $C_{32}H_{28}N_4OS$ requires C, 74.41; H, 5.42; N, 10.85%). IR (Nujol): 3301, 1684, 1606, 1597, 1518, 1502, 1493, 1466, 1448, 1410, 1327, 1300, 1286, 1263, 1207, 1157, 1064, 922, 896, 815, 767 and 692 cm^{-1}. δ ($CDCl_3$): 2.4 (s, 3H), 3.65 (d, 1H, J=18 Hz), 4.25 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 5.8 (d, 1H, J=18 Hz), 7.1-8.5 (m, 20H); m/z (%): 516 (1), 515 (1), 514 (3), 397 (7), 396 (12), 395 (3), 394 (4), 393 (4), 307 (25), 246 (16), 221 (100), 220 (89), 191 (19), 176 (46), 145 (11), 135 (14), 120 (23), 119 (17), 118 (64), 117 (52), 115 (14), 105 (76), 104 (29), 103 (22), 77 (80). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-methoxyphenyl- (80%), m.p. 194-196°C (prisms) (Found: C, 71.89; H, 5.16; N, 10.36; $C_{32}H_{28}N_4O_2S$ requires C, 72.18; H, 5.26; N, 10.52%). IR (Nujol): 3300, 1684, 1603, 1498, 1450, 1408, 1327, 1296, 1253, 1205, 1168, 1024, 922, 898, 833, 760 and 692 cm^{-1}. δ ($CDCl_3$): 3.85 (s, 3H), 3.60 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 5.8 (d, 1H, J=18 Hz), 6.9-8.3 (m, 20 H); m/z (%): 532 (1), 531 (1), 530 (2), 413 (2), 412 (5), 411 (15), 410 (4), 409 (10), 307 (14), 246 (32), 221 (69), 220 (100), 191 (25), 151 (31), 134 (27), 133 (55), 120 (22), 119 (8), 105 (75), 104 (19), 103 (21), 77 (86). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-o-methoxyphenyl- (75%), m.p. 174-175°C (prisms) (Found: C, 72.11; H, 5.41; N, 10.70; $C_{32}H_{28}N_4O_2S$ requires C, 72.18; H, 5.26; N, 10.52%). IR (Nujol): 3279, 1685, 1618, 1599, 1516, 1489, 1467, 1448, 1413, 1363, 1336, 1292, 1250, 1207, 1155, 1105, 1064, 1047, 1026, 756 and 690 cm^{-1}. δ ($CDCl_3$): 3.8 (s, 3H), 3.6 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 5.8 (d, 1H, J=18 Hz), 7.0-8.4 (m, 20H). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-chlorophenyl- (69%) m.p. 143-145°C (prisms) (Found: C, 69.15, H, 4.38; N, 10.20; $C_{31}H_{25}ClN_4OS$ requires C, 69.33; H, 4.65; N, 10.43%). IR (Nujol): 3301, 1681, 1506, 1485, 1462, 1410, 1377, 1321, 1292, 1205, 1157, 1087, 918, 769, 760, 754 and 694 cm^{-1}. δ ($CDCl_3$): 3.55 (d, 1H, J=18 Hz), 4.15 (d, 1H, J=18 Hz), 4.25 (d, 1H, J=18 Hz), 5.75 (d, 1H, J=18 Hz), 7.1-8.4 (m, 20H). m/z (%): 538 (0.4), 537 (0.4), 536 (1), 535 (1), 534 (3), 419 (1), 418 (2), 417 (5), 416 (8), 415 (9), 414 (14), 221 (30), 220 (100), 291 (27), 140 (10), 139 (13), 138 (27), 120 (45), 119 (8), 117 (16), 115 (16), 105 (98), 104 (20), 103 (9), 77 (98). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-nitrophenyl- (60%) m.p. 183-184°C (prisms) (Found: C, 67.78; H, 4.49; N, 12.50; $C_{31}H_{25}N_5O_3S$ requires C, 68.00; H, 4.57; N, 12.79%). IR (Nujol): 3300, 1674, 1618, 1597, 1527, 1506, 1469, 1446, 1412, 1352, 1319, 1304, 1269, 1211, 1155, 1089, 1076, 941, 925, 912, 761, 736 and 692 cm^{-1}. δ ($CDCl_3$): 3.6 (d, 1H, J=18 Hz), 4.2 (d, 1H, J=18 Hz), 4.4 (d, 1H, J=18 Hz), 5.8 (d, 1H, J=18 Hz), 6.8-8.3 (m, 20H).

General Procedure for the Preparation of 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-thiadiazoles. 13. 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-aryl-1,3,4-Δ^2-thiadiazolines 12 (1 mmol) in dry benzene (20 ml) and an equimolecular amount of chloranil were refluxed for 12 h. The solvent was removed under reduced pressure and the resultant aoil was triturated with EtOH. The thiadiazoles obtained were filtered off and recrystallised from ethanol. 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-phenyl- (78%) m.p. 179-181°C (prisms) (Found: C, 74.28; H, 4.61; N, 11.03; $C_{31}H_{24}N_4OS$ requires C, 74.40; H, 4.80; N, 11.20%). IR (Nujol): 1684, 1595, 1579, 1531, 1494, 1466, 1448, 1369, 1319, 1253, 1205, 1060, 1001, 765, 756 and 689 cm^{-1}. δ ($CDCl_3$) 3.8 (d, 1H, J=18 Hz), 4.25 (d, 1H, J=18 Hz), 4.65 (s, 2H), 7.2-8.1 (m, 20H); m/z (%): 500 (10), 381 (80), 380 (13), 379 (38), 309 (4), 307 (2), 292 (2), 276 (3), 220 (21), 219 (1), 191 (2), 120 (13), 119 (6), 105 (100), 104 (2), 103 (19) 77 (96). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-o-methoxyphenyl- (74%), m.p. 212-213°C (needles) (Found: C, 72.20; H, 4.70; N, 10.37; $C_{32}H_{26}N_4O_2S$ requires C, 72.45; H, 4.90 N, 10.56%). IR (Nujol): 1685, 1597, 1583, 1520, 1494, 1464, 1448, 1431, 1377, 1350, 1294, 1259, 1219, 1118, 1070, 1020, 979, 773, 746 and 690 cm^{-1}. δ ($CDCl_3$): 3.8 (s, 3H), 3.85 (d, 1H, J=18 Hz), 4.3 (d, 1H, J=18 Hz), 4.7 (s, 2H), 6.9-8.4 (m, 19H). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-chlorophenyl- (63%), m.p. 132-134°C, (prisms) (Found: C, 69.37; H, 4.16; N, 10.21; $C_{31}H_{23}ClN_4OS$ requires C, 69.59; H, 4.30; N, 10.47%). IR (Nujol): 1687, 1597, 1570, 1516, 1493, 1464, 1448, 1369, 1348, 1302, 1219, 1095, 1062, 1003, 983, 837, 814, 765, 754, 698, 690 and 638 cm^{-1}. δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 4.75 (s, 2H), 7.0-8.2 (m, 19H); m/z (%): 536 (2), 534 (5), 417 (24), 416 (21), 415 (71), 414 (13), 307 (8), 221 (3), 220 (8), 219 (2), 191 (4), 157 (15), 155 (38), 140 (2), 139 (21), 138 (7), 137 (60), 120 (17), 119 (3), 105 (100), 104 (9), 103 (16), 77 (93). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-tolyl- (69%), m.p. 206-208°C (pirsms)

(Found: C, 74.79; H, 4.90; N, 10.70; $C_{32}H_{26}N_4OS$ requires C, 74.70; H, 5.05; N, 10.89%). IR (Nujol): 1685, 1599, 1572, 1518, 1493, 1462, 1448, 1375, 1358, 1224, 1184, 1161, 1118, 1059, 1001, 989, 821, 763, 754, 698 and 690 cm^{-1}. δ ($CDCl_3$): 2.3 (s, 3H), 3.8 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 4.65 (s, 2H), 7.0-8.1 (m, 19 H); m/z (%): 514 (6), 395 (10), 394 (33), 307 (28), 306 (18), 276 (12), 220 (7), 219 (3), 191 (7), 135 (12), 120 (15), 119 (7), 118 (6), 117 (20), 105 (100), 104 (3), 103 (15), 77 (79). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-methoxyphenyl- (81%), m.p. 192-194°C (plates) (Found: C, 72.30; H, 4.76; N, 10.38; $C_{32}H_{26}N_4O_2S$ requires C, 72.45; H, 4.90; N, 10.56%). IR (Nujol): 1684, 1606, 1575, 1518, 1493, 1462, 1466, 1375, 1352, 1305, 1251, 1224, 1174, 1059, 1033, 1001, 979, 837, 761, 754, 690 and 642 cm^{-1}. δ ($CDCl_3$): 3.85 (s, 3H), 3.9 (d, 1H, J=18 Hz), 4.3 (d, 1H, J=18 Hz), 4.75 (s, 2H), 6.9-8.4 (m, 19 H); m/z (%): 530 (5), 411 (16), 410 (13), 109 (24), 307 (15), 207 (11), 191 (4), 151 (29), 134 (27), 133 (55), 120 (21), 119 (4), 105 (86), 104 (3), 103 (20), 77 (100). 2-($\Delta^{2'}$-pyrazolin-1-yl)-5-p-nitrophenyl- (60%), m.p. 221-225°C (plates) (Found: C, 68.03; H, 4.10; N, 12.60; $C_{31}H_{23}N_5O_3S$ requires C, 68.25; H, 4.22; N, 12.84%). IR (Nujol): 1689, 1595, 1533, 1520, 1493, 1462, 1450, 1350, 1084, 1070, 950, 765, 736, 717, 694 and 671 cm^{-1}. δ ($CDCl_3$): 3.8 (d, 1H, J=18 Hz), 4.35 (d, 1H, J=18 Hz), 4.7 (s, 2H), 6.8-8.3 (m, 19 H).

General Procedure for the Preparation of 6-Alkyl- or Arylamido-2,3a,5-triphenylpyrazolo[1,5-c]pyrimidine-7-thione Hydrochlorides. 14. 1-Hydrazinothiocarbonyl-5-phenacyl-3,5-diphenyl-2-pyrazoline 3b (0.414 g, 1 mmol) in dry benzene (30 ml), and an equimolecular amount of acyl chlorides were refluxed for 16 h. The solvent was removed under reduced pressure and the resultant oil was triturated with EtOH. The hydrochlorides obtained were filtered off and recrystallised from EtOH/$CHCl_3$ (1:1). 6-Benzamido- (75%), m.p. 244-246°C (prisms) (Found: C, 69.17; H, 4.42, N, 10.20; $C_{31}H_{25}ClN_4OS$ requires C, 69.33; H, 4.65; N, 10.43%). IR (Nujol): 3296, 1691, 1614, 1599, 1581, 1554, 1462, 1442, 1379, 1352, 1305, 1259, 1086, 1076, 1001, 876, 835, 758, 746, 711, 700 and 690 cm^{-1}. δ ($CDCl_3$): 3.65 (s, 2H), 5.9 (s, 1H), 7.2-8.0 (m, 20H), 9.3 (s, 1H); m/z (%): 501 (M^+-Cl, 1), 469 (3), 468 (7), 423 (1), 323 (2), 322 (2), 280 (2), 279 (10), 245 (3), 221 (4), 220 (7), 219 (6), 191 (6), 179 (2), 178 (4), 128 (7), 121 (15), 120 (2), 117 (6), 115 (12), 105 (100), 104 (24), 103 (34), 77 (86). 6-p-methylbenzamido- (71%), m.p. 278-280°C (prisms) (Found: C, 69.51; H, 4.76; N, 9.98; $C_{32}H_{27}ClN_4OS$ requires C, 69.75, H, 4.90; N, 10.17%). IR (Nujol): 3273, 1701, 1651, 1610, 1562, 1523, 1491, 1458, 1442, 1344, 1321, 1309, 1271, 1253, 1184, 1078, 866, 838, 814, 760, 752, 744, 700 and 692 cm^{-1}. δ ($CDCl_3$): 2.35 (s, 3H), 3.95 (s, 2H), 6.15 (s, 1H), 7.2-8.1 (m, 19 H), 9.3 (s, 1H). m/z (%): 515 (M^+-Cl, 1), 483 (3), 482 (7), 437 (1), 323 (2), 322 (3), 294 (3), 293 (10), 245 (3), 221 (3), 220 (4), 219 (6), 193 (1), 192 (2), 191 (5), 135 (4), 134 (2), 128 (6), 119 (100), 117 (7), 115 (11), 104 (18), 103 (19), 91 (46), 77 (19). 6-p-bromobenzamido- (76%), m.p. 215-216°C, (prisms) (Found: C, 60.12; H, 3.65; N, 8.90; $C_{31}H_{24}BrClN_4OS$ requires C, 60.43; H, 3.89; N, 9.09%). IR (Nujol): 3245, 1703, 1664, 1593, 1510, 1464, 1444, 1377 1352, 1305, 1248, 1080, 1012, 856, 837, 812, 768 and 690 cm^{-1}. δ ($CDCl_3$): 3.75 (s, 2H), 6.0 (s, 1H), 7.4-8.0 (m, 19H), 9.5 (s, 1H); m/z (%): 581 (M^++2-Cl, 3), 579 (M^+-Cl, 3), 549 (5), 548 (13), 547 (5), 546 (13), 503 (3), 501 (3), 360 (3), 359 (11), 358 (3), 357 (11), 323 (8), 321 (11), 259 (2), 258 (11), 257 (2), 256 (11), 245 (8), 221 (99), 220 (100), 219 (12), 201 (6), 200 (11), 199 (7), 198 (11), 191 (21), 185 (37), 183 (49), 157 (16), 155 (17), 128 (5), 117 (8), 115 (9), 104 (16), 103 (14), 77 (40). 6-p-chlorobenzamido- (61%), m.p. 218-219°C (prisms) (Found: C, 65.00; H, 4.32; N, 9.61; $C_{31}H_{24}Cl_2N_4OS$ requires C, 65.14; H, 4.20; N, 9.80%). IR (Nujol): 3262, 1697, 1597, 1464, 1444, 1377, 1350, 1307, 1248, 1089, 1016, 856, 835, 812, 763, 721 and 690 cm^{-1}. δ ($CDCl_3$): 3.8 (s, 2H), 6.0 (s, 1H), 7.4-8.1 (m, 19H), 9.6 (s, 1H); m/z (%): 537 (M^++2-Cl, 0.6), 535 (M^+-Cl, 2), 505 (0.6), 504 (2), 503 (2), 502 (5), 459 (0.6), 457 (2), 323 (2), 322 (5), 316 (1), 315 (3), 314 (3), 313 (10), 245 (5), 221 (7), 220 (8), 219 (7), 214 (3), 212 (7), 157 (3), 156 (1), 155 (7), 154 (2), 141 (33), 139 (100), 128 (9), 117 (7), 115 (16), 113 (15), 111 (40), 104 (31), 103 (29), 77 (31). 6-acetamido- (65%), m.p. 255-257°C. (prisms) (Found: C, 65.90; H, 4.71; N, 11.60 $C_{26}H_{23}ClN_4OS$ requires C, 65.75; H, 4.84; N, 11.80%). IR (Nujol): 3324, 1711, 1653, 1504, 1491, 1454, 1440, 1358, 1309, 1255, 1089, 868, 839, 819, 763, 756, and 698 cm^{-1}. δ ($CDCl_3$): 2.3 (s, 3H), 3.8 (s, 2H), 6.1 (s, 1H), 7.0-8.1 (m, 15H), 9,35 (s, 1H). m/z (%): 439 (M^+-Cl, 13), 407 (5), 406 (29), 405 (100), 361 (23), 323 (9), 322 (15), 245 (13), 221 (9), 220 (6), 219 (8), 218 (13), 217 (32), 191 (6), 218 (5), 117 (3), 116 (4), 115 (7), 104 (9), 103 (14), 77 (18), 43 (26).

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REFERENCES

1. A.T.Balaban et al. Adv. Heterocyclic Chem., Suppl. 2 (1982).
2. A.R.Katritzky, P.Ballesteros, A.Tárraga Tomás, J.Chem.Soc. Perkin Trans. I 1981, 1495.
3. E.A.Zvezdina, G.N.Dorofeenko, Khim.Geterotsikl. Soedin, 5, 695 (1983).
4. P.Molina, A.Tárraga, M.Lorenzo Peña, Synthesis, 1984, 697.
5. D.M.Evans, D.R.Taylor, J.Chem.Soc. Chem. Commun., 1982, 188
6. M.Lempert-Streter, K.Lempert, J.Moller, J.Chem.Soc. Perkin Trans. I, 1983 2011.