Synthesis of Tetrahydrothiopyrano[3,2-*c*]pyrazole Derivatives from 3-Thianones

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The synthesis of bicyclic pyrazoles and pyrazolones in which the fused ring contains a sulfur atom in different oxidation states is reported.

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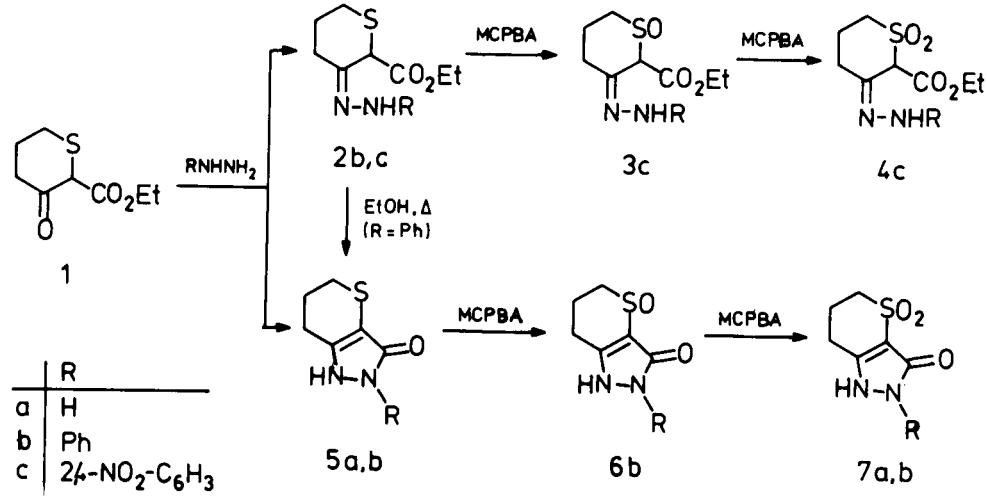
The pyrazole and pyrazolone rings, particularly when fused to carbocyclic rings, are of interest in the chemical and pharmaceutical industry as herbicides [1] and analgesics [2]. Recently the fusion of the pyrazole system with the thiopyran ring has led to products of interest for their use as antiflogists [3] and photosensitizers [4]. As it is a few years since we have been dealing with thiopyran derivatives [5] we have used these compounds as substrates for the synthesis of bicyclic pyrazole and pyrazolone systems.

The ketosulfide **1** [6,7] was reacted with hydrazine, phenylhydrazine and 2,4-dinitrophenylhydrazine (Scheme 1). Only the pyrazolone derivatives **5a** [8] and **5b** [4,8] were formed, whereas the reaction with the deactivated hydrazine led to the aryl hydrazone **2c**, which however did not cyclize under any conditions of *p*H and temperature. Also the phenylhydrazone **2b** could be separated, which on the contrary underwent cyclization to the corresponding pyrazolone derivative **5b** in basic medium. The phenylhydrazones, whose stereochemistry was not assigned, were single diastereoisomers, differently from what found for the phenylhydrazones of linear β-ketoesters [9], which were always pairs of diastereoisomers. As to the structure of the pyrazolones, they have depicted in the NH form [10], although a tautomeric equilibrium between the OH and the NH forms might be envisaged. The position of this equilibrium however could not be determined, owing to the insolubility of the products in the usual solvents [11]. The third possible tautomer, *i.e.* the CH form is surely absent, at least in the solid state, as indicated by the absence of the C=O absorption in the range 1720-1700 cm^{-1}.

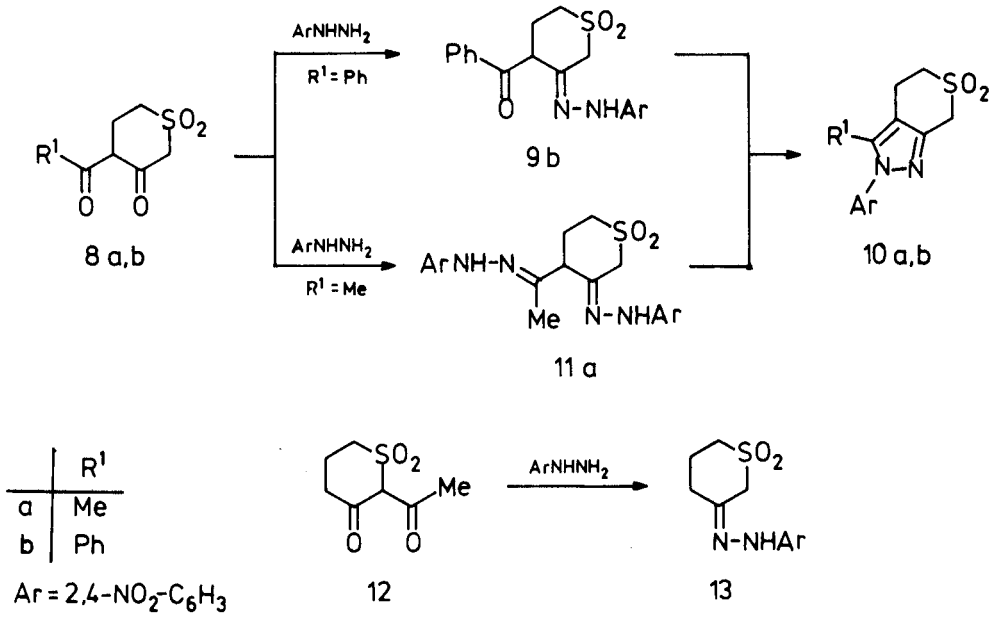
Attempts to oxidize both the hydrazone derivatives **2** and the pyrazolone derivatives **5** have also been made. The monooxidation by *m*-chloroperbenzoic acid in fact allowed the only isolation of the sulfoxide derivatives **3c** and **6b**, respectively, whereas **2b** gave complicated mixtures of unidentified products and **5a** led directly to the sulfone derivative **7a**. Neither in this case the hydrazone derivative **3c** underwent cyclization to the corresponding pyrazolone system. The exhaustive oxidation of the same substrates **2** and **5** led to the corresponding sulfone derivatives **4c** and **7a,b** respectively. The hydrazone system **4c** again failed to cyclize into the corresponding pyrazole derivative. An attempt was also made to prepare the products which are missing in the Scheme by previous oxidation of the parent ketosulfide **1**, but only cleavage products were obtained also under very mild conditions.

As we had also the availability of some acylated ketosulfones, namely **8** and **12** [5], we reacted them with

Scheme 1



Scheme 2

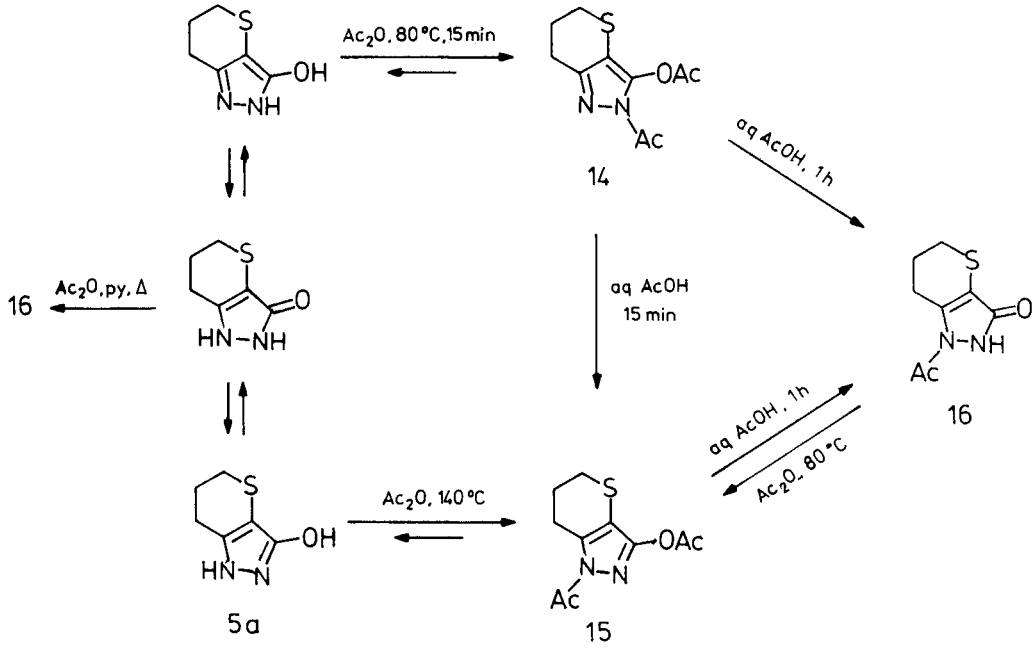


2,4-dinitrophenylhydrazine with the aim of preparing pyrazole derivatives (Scheme 2).

The reaction succeeded with the 4-acylated compounds **8a** and **8b**, which furnished the pyrazole derivatives **10a** and **10b** respectively, through the corresponding 2,4-dinitrophenylhydrazone intermediates, but only the compound **9b** could be separated. In the case of **8a** only the *bis*-hydrazone **11a** was separated, which cyclized with loss of one mole of 2,4-dinitrophenylhydrazine, as was evident also by the mass spectrum. The thermal cyclization of **11a** to **10a** in fact occurred prior to ionization and the resulting spectrum was identical with that of the pure **10a**.

On the contrary, the 2-acetylketosulfone **12** failed to react in the usual manner. Under the acidic conditions

Scheme 3



used, the molecule lost the acetyl group, probably as ketene [5], and the resulting heterocyclic ketone reacted with the hydrazine to give the corresponding hydrazone derivative **13**, besides small amounts of other acyclic compounds not further studied.

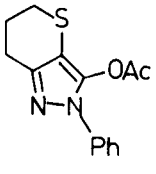
It is worthwhile to make a comparison with analogous reactions carried out by Jacquier and coworkers on the corresponding carbocyclic systems [12], particularly as far as the regioselectivity of the reactions is concerned. In fact two isomeric pyrazoles were formed in that case, in ratio 3:1 deriving from the prevalent attack of 2,4-dinitrophenylhydrazine on the ring carbonyl group. On the contrary, in the present case the only regioisomer formed was the pyrazole system **10** in both cases, owing to the activating effect exerted by the sulfonyl group on the ring carbonyl group towards the nucleophilic attack.

The acetylation reaction of the pyrazolone **5a** deserves a particular comment (Scheme 3).

In fact when it was carried out with acetic anhydride at 80° for 15 minutes, the double acetylated product **14** was formed, as indicated by the presence of two carbonyl absorption bands at 1790 and 1725 cm^{-1}. All these attributions have been made by comparison of the ir spectra of our acetylated pyrazoles with those prepared by Weissberger and Porter [13], which we reprepared and analysed. Compound **14** was a product of kinetic formation as it isomerized into **15**, by reflux in aqueous acetic acid for 15 minutes, as indicated by the absorption values of its carbonyl stretching bands at 1775 and 1720 cm^{-1}. The correctness of the structural attributions to the regioisomers **14** and **15** was also confirmed by their nmr spectra. The heterocyclic protons of **15** in fact resonate in a narrower range (3.5-2.8 ppm) than **14** (3.5-2.5 ppm), as a result of a slight deshielding effect of the acetyl group at N-1 in **15**.

The same compound **15** could be attained to directly from **5a** when the acetylation was performed at 140°. Both isomers **14** and **15** were *O*-deacetylated by heating in aqueous acetic acid for 1 hour, to yield the *N*-acetyl derivative **16**, whose carbonyl absorption band appeared at 1710 cm^{-1} [14]. This product could also be obtained by reacting the substrate **5a** with acetic anhydride in refluxing pyridine.

On the contrary, acetylation of **5b** led to the corresponding *O*-acetyl derivative **17** under any conditions.



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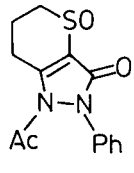

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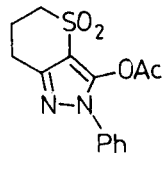

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Also the acetylation of the corresponding sulfone derivative **7b** furnished the *O*-acetyl derivative **19**. Both compounds are in fact characterized by the acetyloxy stretching band at about 1800 cm^{-1}. Unexpectedly, the same reaction carried out on the sulfoxide derivative **6b** gave the product **18** whose spectroscopic data are quite different from those of **17** and **19**. Its ir carbonyl stretching band in fact appeared at 1740 and 1710 cm^{-1}, values which are consistent with the structure of an *N*-acetyl derivative, as assigned. The lack of *O*-acetylation of the substrate **18** could be explained admitting that the sulfoxide group is the first site of reversible acetylation. This group would inhibit the subsequent *O*-acetylation for steric reasons and it would direct the acetylation towards the nitrogen atom.

EXPERIMENTAL

Melting points were determined with a Büchi capillary apparatus and are uncorrected. Infrared spectra (nujol mulls unless otherwise indicated) were taken on a Perkin-Elmer 1320 spectrometer. Nuclear Magnetic Resonance Spectra were determined for solutions in deuteriochloroform unless otherwise stated with TMS as internal standard using a Bruker 80 WP or Varian 360 A spectrometer. The mass spectra were obtained on a VG 7070 spectrometer at 70 eV. Preparative thin layer chromatography was performed on 20 x 20 cm silica gel G plates, 0.5 mm in thickness. Column chromatography was carried out by the flash chromatography technique with Merck silica gel for column chromatography (0.040-0.63 mm mesh).

2,5,6,7-Tetrahydrothiopyrano[3,2-*c*]pyrazole-3(1*H*)-one (**5a**).

The ketosulfide **1** (0.35 g, 2.0 mmoles) and hydrazine hydrate in excess were refluxed for 1 hour. The solid precipitated, **5a**, was filtered off, mp 272° (lit [7] 274°); ir: 3100-2000 (NH or OH), 1630, 1580, 1550 cm^{-1} (C=C, C=N); ^1H nmr (deuteriotrifluoroacetic acid): δ 10.2 (2H, s, trifluoracetic acid exchanged with 2 NH), 3.3-2.8 (4H, m, $CH_2CH_2CH_2S$), 2.6-2.1 ppm (2H, m, $CH_2CH_2CH_2S$); ms: M^+ 156 (100), 149 (5), 128 (35).

5,6-Dihydro-2-ethoxycarbonyl-2*H*-thiopyran-3(4*H*)-one 3-Phenylhydrazone (**2b**).

The ketosulfide **1** (1.14 g, 6.0 mmoles) was reacted with phenylhydrazine hydrochloride (0.87 g, 6.0 mmoles) in a mixture of ethanol (45 ml) and water (10 ml), in the presence of sodium carbonate (0.66 g, 6.0 mmoles). After heating for 15 minutes the solution was concentrated and left in the refrigerator for 12 hours. The solid **2b** (0.88 g, yield 52%) was filtered and washed repeatedly with ethanol, mp 101-102°; ir: 3350 (NH), 1710 (C=O), 1605 (C=N), 1600 cm^{-1} (Ph); ^1H nmr: δ 7.6-6.7 (6H, m, Ph, NH), 4.3 (2H, q, CH_2Me), 4.2 (1H, s, CHS), 3.2-1.5 (6H, m, $(CH_2)_3$), 1.2 (3 H, t, Me).

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.20; H, 6.49; N, 10.02.

The remaining product (yield 22%) was the pyrazolone **5b**.

2-Phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one (**5b**).

A solution of sodium (0.26 g) in absolute ethanol (30 ml) was added to a solution of the phenylhydrazone **2b** (0.2 g, 0.86 mmole) in benzene (4 ml). The mixture was refluxed for 1 hour, acidified with acetic acid and concentrated. The solid **5b** (0.14 g, yield 87%) was filtered and crystallized from aqueous ethanol, mp 172°; ir: 3000-2000 (NH or OH), 1620, 1570 (C=C, C=N), 1595, 1490 cm^{-1} (Ph); ^1H nmr (deuteriotrifluoroacetic acid): δ 11.4 (2H, s, trifluoroacetic acid exchanged with 2 NH), 7.8 (5H, m, Ph), 2.8-2.3 (4H, m, $CH_2CH_2CH_2$), 2.7-2.0 (2H, m, $CH_2CH_2CH_2$); ms: M^+ 232 (100), 127 (50).

Anal. Calcd. for $C_{12}H_{12}N_2OS$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.01; H, 5.26; N, 11.98.

5,6-Dihydro-2-ethoxycarbonyl-2*H*-thiopyran-3(4*H*)-one 3-(2',4'-Dinitrophenyl)hydrazone (**2c**).

The ketosulfide **1** (0.35 g, 2.0 mmoles) and 2,4-dinitrophenylhydrazine (0.40 g, 2.0 mmoles) were heated for 15 minutes in the presence of concentrated sulfuric acid (0.1 ml). The resulting product, **2c** (0.50 g, yield 68%) was crystallized from ethanol, mp 129-131°; ir: 3330 (NH), 1735 (CO), 1620 (C=N), 1590 cm^{-1} (Ar); ^1H nmr: δ 11.5 (1H, bs, NH), 9.3 (1H, m, *m*-Ar), 8.5-8.0 (2H, m, *o*-, *m*-Ar), 4.6 (2H, q, CH_2Me), 4.5 (1H, s, CHS), 3.0-2.0 (6H, m, $(CH_2)_3$), 1.4 (3H, t, Me); ms: M^+ 368 (20), 333 (20), 295 (100).

Anal. Calcd. for $C_{14}H_{16}N_4O_6S$: C, 45.66; H, 4.38; N, 15.21. Found: C, 45.59; H, 4.31; N, 15.19.

Oxidation Reactions.

The oxidations were carried out with *m*-chloroperbenzoic acid in ratio 1:1 or 1:2, in methanol or in chloroform at room temperature for 6-24 hours. The solvent was eliminated and the crude was washed with ethanol.

5,6-Dihydro-2-ethoxycarbonyl-2*H*-thiopyran-3(4*H*)-one 3-(2',4'-Dinitrophenyl)hydrazone 1-Oxide (**3c**).

Compound **3c** had mp 115° (washed with methanol); ir: 3310 (NH), 1725 (C=O), 1610 (C=N), 1590 (Ar), 1510, 1335 (NO_2), 1050 cm^{-1} (SO); ^1H nmr: δ 11.6 (1H, bs, NH), 9.3 (1H, m, *m*-Ar), 8.7-8.0 (2H, m, *o*-, *m*-Ar), 4.8 (1H, bs, CHSO), 4.4 (2H, q, CH_2Me), 4.0-2.0 (6H, m, $(CH_2)_3$), 1.4 (3H, t, Me); ms: M^+ 384 (2), 366 (100), 320 (55).

Anal. Calcd. for $C_{14}H_{16}N_4O_7S$: C, 47.76; H, 4.20; N, 14.58. Found: C, 47.60; H, 4.18; N, 14.53.

5,6-Dihydro-2-ethoxycarbonyl-2*H*-thiopyran-3(4*H*)-one 3-(2',4'-Dinitrophenyl)hydrazone 1,1-Dioxide (**4c**).

The compound **4c** had mp 185°, from ethanol; ir: 3310 (NH), 1720 (C=O), 1615 (C=N), 1595 (Ar), 1515, 1335 (NO_2), 1300, 1200 cm^{-1} (SO_2); ^1H nmr: δ 11.2 (1H, bs, NH), 9.4 (1H, m, *m*-Ar), 8.7-8.0 (2H, m, *o*-, *m*-Ar), 4.9 (1H, bs, $CHSO_2$), 4.4 (2H, q, CH_2Me), 4.2-2.2 (6H, m, $(CH_2)_3$), 1.3 (3H, t, Me); ms: M^+ 400 (20), 354 (50), 311 (30), 290 (100).

Anal. Calcd. for $C_{14}H_{16}N_4O_8S$: C, 42.01; H, 4.03; N, 14.00. Found: C, 41.80; H, 4.08; N, 13.95.

2-Phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one 4-Oxide (**6b**).

The product **6b** had mp 125-126°; ir: 2700-2400 (NH or OH), 1550, 1520 (C=C, C=N), 1590, 1490 (Ar), 970 cm^{-1} (SO); ^1H nmr: δ 9.2 (1H, m, NH), 7.5 (5H, m, Ph), 3.5-2.0 (6H, m, $(CH_2)_3$); ms: M^+ 248 (17), 232 (26), 77 (100).

Anal. Calcd. for $C_{12}H_{12}N_2O_3S$: C, 58.06; H, 4.87; N, 11.28. Found: C, 58.00; H, 4.83; N, 11.20.

2,5,6,7-Tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one 4,4-Dioxide (**7a**).

The product **7a** had mp 285° dec, from methanol: ir: 3000-2000 (NH or OH), 1630, 1600, 1550, 1520 (C=C, C=N), 1280, 1125 cm^{-1} (SO_2); ^1H nmr: insoluble; ms: M^+ 188 (100), 124 (17), 123 (17), 122 (17), 96 (42).

Anal. Calcd. for $C_6H_8N_2O_3S$: C, 38.30; H, 4.29; N, 14.89. Found: C, 38.45; H, 4.33; N, 14.82.

2-Phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one 4,4-Dioxide (**7b**).

The product **7b** had mp 258-260°, from methanol; ir: 2750-2000 (NH or OH), 1635, 1550 (C=C, C=N), 1590, 1500, 1490 (Ph), 1305, 1290, 1120 cm^{-1} (SO_2); ^1H nmr: insoluble; ms: M^+ 264 (100), 200 (13).

Anal. Calcd. for $C_{12}H_{12}N_2O_3S$: C, 54.55; H, 4.58; N, 10.60. Found: C, 54.40; H, 4.60; N, 10.54.

2-(2',4'-Dinitrophenyl)-3-methyl-2,4,5,7-tetrahydrothiopyrano[3,4-*c*]-pyrazole 6,6-Dioxide (**10a**).

Compound **8a** (0.1 g, 0.52 mmole) was heated in refluxing methanol (25 ml) with 2,4-dinitrophenylhydrazine (0.1 g, 0.52 mmole) and concentrated hydrochloric acid (0.1 ml) for 1 hour. The crude mixture was chromatographed on preparative tlc (eluent: benzene:ethanol 95:5). Compound **10a** was separated, mp 198°, from ethanol; ir: 1605 (Ar), 1540 (NO_2), 1350-1330 (NO_2 and SO_2), 1130 cm^{-1} (SO_2); ^1H nmr: δ 9.0-7.5 (3H, s, Ar), 4.4 (2H, s, CH_2SO_2), 3.3 (4H, m, CH_2CH_2), 2.3 (3H, s, Me); ms: M^+ 352 (4), 351 (30), 288 (30), 287 (32), 43 (100).

Anal. Calcd. for $C_{12}H_{12}N_4O_6S$: C, 42.36; H, 3.55; N, 16.47. Found: C, 42.40; H, 3.58; N, 16.43.

The other product was identified as 5-acetyl-5,6-dihydro-2*H*-thiopyran-3(4*H*)-one *bis*-(2,4-dinitrophenyl)hydrazone 1,1-dioxide, **11a**, mp 250-251°; ir: 3310, 3295 (NH), 1615 (C=N), 1590 cm^{-1} (Ar). ^1H nmr: insoluble.

Anal. Calcd. for $C_{19}H_{18}N_8O_{10}S$: C, 41.48; H, 3.24; N, 20.36. Found: C, 41.40; H, 3.20; N, 20.25.

The latter compound (0.05 g) was heated in ethanol with sulfuric acid (1 ml) for 16 hours, to give the pyrazole derivative **10a**.

5,6-Dihydro-2*H*-thiopyran-3(4*H*)-one 3-(2',4'-Dinitrophenyl)hydrazone 1,1-Dioxide (**13**).

Compound **12** (0.15 g, 0.74 mmole) was heated in refluxing ethanol (20 ml) with (2,4-dinitrophenyl)hydrazine (0.15 g, 0.74 mmole) and hydrochloric acid (0.2 ml) for 1 hour. After elimination of the solvent the product **13** (0.13 g, yield 50%) was isolated by preparative chromatography, mp 168°; ir: 3325 (NH), 1610 (C=N), 1595 (Ar), 1535, 1335 (NO_2), 1305, 1135 cm^{-1} (SO_2); ^1H nmr: insoluble; ms: M^+ 328 (15), 294 (2), 247 (20), 32 (100).

Anal. Calcd. for $C_{11}H_{12}N_4O_6S$: C, 40.25; H, 3.68; N, 17.07. Found: C, 40.21; H, 3.70; N, 17.09.

4-Benzoyl-5,6-dihydro-2*H*-thiopyran-3(4*H*)-one (2',4'-Dinitrophenyl)hydrazone 1,1-Dioxide (**9b**).

The ketosulfone **8b** (0.1 g, 0.4 mmole) was suspended in an excess of ethanolic solution of 2,4-dinitrophenylhydrazine (0.4 g, 2.0 mmoles) with sulfuric acid (2 ml). The mixture was left at room temperature for 1 hour. The crystalline product obtained, **9b**, was crystallized from ethanol, mp 175°; ir: 3300 (NH), 1675 (C=O), 1620 (C=N), 1590 (Ph), 1530, 1370, 1340 (NO_2), 1310, 1130 cm^{-1} (SO_2); ^1H nmr: δ 8.3-7.2 (9H, m, Ar, Ph, NH), 4.5 (2H, bs, CH_2S), 3.7-3.2 (3H, m, $CH_2CH_2SO_2$, CH), 3.2-2.6 (2H, m, $CH_2CH_2SO_2$); ms: the product cyclized to **10b** at 230°.

Anal. Calcd. for $C_{18}H_{16}N_4O_6S$: C, 50.00; H, 3.70; N, 12.96. Found: C, 50.12; H, 3.72; N, 12.92.

2-(2',4'-Dinitrophenyl)-3-phenyl-2,4,5,7-tetrahydrothiopyrano[3,4-*c*]-pyrazole (**10b**).

The ketosulfone **8b** was added to the 2,4-dinitrophenylhydrazine solution as in the previous reaction and the mixture heated for 15 minutes. Water was added, the red-orange solid was filtered off and purified on preparative tlc. The compound **10b** was isolated, mp 154°, from methanol; ir: 1605 (Ph), 1530, 1340 (NO_2), 1315, 1295, 1120 cm^{-1} (SO_2); ^1H nmr: δ 8.9-8.3 (2H, m, *o*-Ph) 7.6-7.0 (6H, m, *m*-, *p*-Ph, Ar), 4.4 (2H, s, CH_2SO_2), 3.3 (4H, m, CH_2CH_2); ms: M^+ 414 (19), 350 (55), 349 (56), 302 (24).

Anal. Calcd. for $C_{18}H_{14}N_4O_6S$: C, 52.17; H, 3.38; N, 13.52. Found: C, 52.10; H, 3.40; N, 13.59.

Acetylation Reactions.

2-Acetyl-3-acetyloxy-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazole (**14**).

The pyrazolone **5a** (0.20 g, 1.3 mmoles) was refluxed in an excess of acetic anhydride in a water bath for 15 minutes. The mixture was poured into iced water under stirring and the solid separated, **14** (0.21 g, yield 65%), mp 99-100°, from light petroleum; ir: 1790 (OCOMe), 1730 (NCOMe), 1595 cm^{-1} (Ar); ^1H nmr: δ 3.5-2.5 (7H, m and s, CH_2CH_2CH_2S, OCOMe), 2.6 (s, OCOMe), 2.5-2.0 (5H, m and s, $CH_3CH_2CH_2S$, NCOMe), 2.3 (s, NCOMe); ms: M^+ 240 (1), 198 (30), 156 (100).

Anal. Calcd. for $C_{10}H_{12}N_2O_3S$: C, 50.04; H, 5.04; N, 11.66. Found: C, 49.96; H, 4.99; N, 11.70.

1-Acetyl-3-acetyloxy-1,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazole (**15**).

The pyrazolone **5a** (0.40 g, 2.55 mmoles) was refluxed in an excess of

acetic anhydride for 1 hour. Elimination of the solvent left an oil, **15**, which was crystallized from light petroleum, mp 109-111° (0.55 g, yield 89%); ir: 1775 (OCOMe), 1720 (NCOMe), 1590, 1570 cm^{-1} (Ar); ^1H nmr: δ 3.5-2.8 (4H, m, $CH_2CH_2CH_2S$), 2.6 (3H, s, OCOMe), 2.4-2.0 (5H, m and s, CH_2CH_2S, NCOMe), 2.4 (s, NCOMe); ms: M^+ 240 (16), 198 (30), 156 (100).

Anal. Calcd. for $C_{10}H_{12}N_2O_3S$: C, 50.04; H, 5.04; N, 11.66. Found: C, 49.91; H, 4.96; N, 11.74.

1-Acetyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one (**16**).

The pyrazolone **5a** (0.16 g, 1.0 mmole) was suspended in pyridine (2 ml) and acetic anhydride (0.1 ml) was added. The mixture was refluxed for 50 minutes and water was then added. The compound **16** was separated (0.11 g, yield 54%), mp 216°; ir: 2720-2500 (NH or OH), 1710 (NCOMe), 1590, 1525 cm^{-1} (C=C, C=N); ^1H nmr: insoluble; ms: M^+ 198 (26), 156 (100).

Anal. Calcd. for $C_8H_{10}N_2O_2S$: C, 48.49; H, 5.09; N, 14.14. Found: C, 48.20; H, 4.96; N, 14.07.

The same product **16** was obtained by refluxing the acetylated pyrazolones **14** and **15** in 66% acetic acid for 1 hour. The monoacetyl pyrazolone **16** was acetylated by acetic anhydride in water bath for 40 minutes to give the corresponding compound **15**.

3-Acetyloxy-2-phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazole (**17**).

The pyrazolone **5b** (0.1 g, 0.43 mmole) was refluxed in acetic anhydride for 1 hour. The residue was crystallized from light petroleum to give compound **17** (0.07 g, yield 63%), mp 71-73°; ir: 1790 (OCOMe), 1600, 1555 cm^{-1} (Ar); ^1H nmr: δ 7.5 (5H, m, Ph), 3.2-2.7 (4H, m, $CH_2CH_2CH_2S$), 2.6-2.0 (5H, m and s, $CH_2CH_2CH_2S$, COMe), 2.3 (s, Me); ms: M^+ 274 (9), 232 (100).

Anal. Calcd. for $C_{14}H_{14}N_2O_2S$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.40; H, 5.20; N, 10.16.

1-Acetyl-2-phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazol-3(1*H*)-one 4-Oxide (**18**).

Acetylation of the pyrazolone **6b** was carried out as above, to yield the compound **18**, mp 138°, from benzene-light petroleum; ir: 1740 (COMe), 1710 (C=O), 1615, 1590 (Ph), 965 cm^{-1} (SO); ^1H nmr: δ 8.2-7.0 (5H, m, Ph), 4.0-2.0 (9H, m and s, $(CH_2)_3$, COMe), 2.2 (s, COMe); ms: M^+ 290 (37), 248 (17), 231 (63), 77 (100).

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: C, 57.93; H, 4.86; N, 9.65. Found: C, 58.10; H, 4.90; N, 9.59.

3-Acetyloxy-2-phenyl-2,5,6,7-tetrahydrothiopyrano[3,2-*c*]pyrazole 4,4-Dioxide (**19**).

Acetylation of compound **7b**, carried out as above gave the corresponding derivative **19**, mp 135°, from light petroleum; ir: 1800 (OCOMe), 1590 (Ph), 1300, 1255, 1150 cm^{-1} (SO_2); ^1H nmr: δ 7.6 (5H, m, Ph), 3.5-2.0 (9H, m and s, $(CH_2)_3$, COMe), 2.3 (s, Me); ms: M^+ 306 (8), 264 (100), 200 (6).

Anal. Calcd. for $C_{14}H_{14}N_2O_4S$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.88; H, 4.57; N, 9.10.

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