thiourea (2), excellent yields of 4-arylmethyl-3-mercapto-6-methylpyridazines 5 were directly formed without the isolation of any thiuronium salts 3, thought to be intermediates in this reaction.

\[
\begin{align*}
1a & : \quad \text{Ar} \quad \text{Cl} \\
1b & : \quad \text{Ar} \quad \text{H}_2\text{C} \quad \text{-} \\
1c & : \quad \text{Ar} \quad \text{Cl} \quad \text{-} \\
2 & \\
3 & \\
4 & \\
5 & \\
6 & \\
5a-c & \\
7b &
\end{align*}
\]

The structures of the products were inferred from microanalytical data and by comparison with the products 5 obtained by the action of phosphorus pentasulphide on 4-arylmethyl-6-methylpyridazin-3(2H)-ones 6.

The following evidence is in favour of the 3-mercaptopyridazine structure 5 and not its tautomeric structure 4: (a) The I.R. spectra lack the bands characteristic of NH and C=S stretching frequencies; (b) compound 5b was easily oxidised to the disulphide 7b by iodine solution.

(c) The products react with dimethyl sulphate to give the S-methyl derivatives 8a–c, the structures of which were substantiated by microanalytical data and the absence of the C=S band in the I.R. spectra. Further confirmation is given by the fact that 8a and 8c are different from 4-arylmethyl-2,6-dimethylpyridazin-3(2H)-thiones 9a and 9b, obtained by the action of phosphorus pentasulphide on the corresponding 4-arylmethyl-2,6-dimethylpyridazin-3(2H)-one (9, Y = O). Product 5b was also easily alkylated by ethyl iodide to give the S-ethyl derivative 8d.

Recently, it was reported that 6-arylpurazin-3(2H)-ones react in the lactam form with acrylonitrile to give N-cyanoethyl derivatives. The present investigation was ex-
tended to involve the reaction of 5b and 5c with acrylonitrile, which gave good yields of the S-(2-cyanoethyl) derivatives 10b and 10c.

The structures of 10 were confirmed by microanalytical data, the presence of sharp bands characteristic of \( \text{C=}\text{N} \) stretching frequencies and lack of those characteristic of the C=S group in the I.R. spectra, and the fact that attempted hydrolysis by heating under reflux with aqueous sodium hydroxide solution did not lead to the formation of the expected acid but resulted in cleavage of the cyanoethyl group to give 4-aryl methyl-3-mercapto-6-methylpyridazines 5. This observation excludes an N-cyanoethyl structure 11, since compounds of this type undergo hydrolysis easily to give the corresponding acids². Moreover, this observation is not unusual since some related systems behave similarly. Thus, it was reported that while \( N \)-methylthioquinazolones are not cleaved, the \( S \)-methyl isomers are easily cleaved under the influence of acid³.

When 4-aryl methyl-6-methylpyridazine-3(2H)-ones 6 were allowed to react with acrylonitrile under similar conditions the reaction gave 4-aryl methyl-2-(2'-cyanoethyl)-6-methylpyridazin-3(2H)-ones 12.

The structures of 12 were confirmed by microanalytical data and by the presence in the I.R. spectra of sharp bands at wavelengths characteristic of \( \nu_{\text{C=N}} \) in addition to strong bands in the region characteristic of carbonyl stretching frequencies of cyclic amides. Product 12b is easily hydrolysed to the corresponding acid 13b by boiling aqueous sodium hydroxide. The acid 13 dissolves in carbonate solution and precipitates on acidification. Its I.R. spectrum shows a broad band in the region characteristic of \( \nu_{\text{OH}} \) of carboxylic acids in addition to the carbonyl stretching frequencies of both cyclic amides and carboxylic acids.

<table>
<thead>
<tr>
<th>Table. Compounds 5, 8, 9, 10, and 12 prepared</th>
</tr>
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<tbody>
<tr>
<td><strong>Product</strong></td>
</tr>
<tr>
<td>5a</td>
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<tr>
<td>5b</td>
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<tr>
<td>5c</td>
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<tr>
<td>8a</td>
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<td>8b</td>
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<td>8d</td>
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<td>9a</td>
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<td>10b</td>
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<tr>
<td>12a</td>
</tr>
<tr>
<td>12b</td>
</tr>
<tr>
<td>12c</td>
</tr>
</tbody>
</table>

* All compounds gave satisfactory microanalyses (C ± 0.40, H ± 0.36, N ± 0.50, Cl ± 0.45, S ± 0.7) exceptions: 9a, 12a: C ± 0.68, 8c, 8d, 9b.

N = 0.73, 5a, 5b, 5c, 12a: S = 0.79.

* No C, H analysis available.
All melting points are uncorrected. I.R. spectra were measured on a Pye Unicam 1200 and Unicam SP 200 G using the KBr disc technique. Analyses were carried out in the Research Microanalytical Laboratories of El-Nasr Company for Pharmaceutical Chemicals.

4-Arylmethyl-3-mercapto-6-methylpyridazines 5:
Method A: Thiourea (2. 91 g, 0.012 mol) is added to a solution of 4-arylmethyl-3-chloro-6-methylpyridazines 1a-c (0.01 mol) in ethanol (30 ml) and the mixture is heated under reflux for 5 h. The yellow solid obtained after cooling is crystallised from benzene to give 5; yield: 80-90%.

Method B: To a solution of 4-arylmethyl-6-methylpyridazin-3(2H)-one 6 (0.01 mol) in xylene (30 ml), phosphorus pentasulphide (3.33 g, 0.015 mol) is added and the mixture is heated under reflux for 10 h. After cooling, the reaction mixture is extracted with 10% aqueous sodium hydroxide solution (20 ml). The alkaline extracts are cooled and concentrated hydrochloric acid (~5 ml) is added till the mixture is just acidic. The yellow solids which separate are filtered off and crystallised from benzene to give 5; yield: 25-30%.

Bis[6-methyl-4-(p-methylbenzyl)-3-pyridazinyl] Disulphide (7b):
A solution of iodine (5.08 g, 0.02 mol) in 5% potassium iodide solution (100 ml) is added drop-wise with stirring to a solution of 5b (2.3 g, 0.01 mol) in 10% aqueous sodium hydroxide (10 ml) until the colour of iodine persists. The solid formed is filtered off and crystallised from benzene to give 7b as colourless crystals; yield: 0.73 g (32%); m.p. 168°C.

C₁₂H₁₅N₂S₂ calc. N 12.23 S 13.97
(458.5) found 11.46 14.20

4-Arylmethyl-6-methyl-3-methylthiopyridazines 8a-c:
Dimethyl sulphate (1.89 g, 0.015 mol) is added dropwise to a solution of 4-arylmethyl-3-mercapto-6-methylpyridazine 5 (0.01 mol) in 10% aqueous sodium hydroxide (10 ml) and the mixture is warmed for a few minutes. The pale yellow solids formed are filtered off and crystallised from light petroleum ether (b.p. 60-80°C) to give 8a-c; yield: 72-83% (Table).

3-Ethylthio-4-(p-methylbenzyl)-6-methylpyridazine (8d):
3-Mercapto-4-(p-methylbenzyl)-6-methylpyridazine (5b, 2.3 g, 0.01 mol), dissolved in the minimum amount of 10% ethanolic sodium hydroxide (~10 ml), is treated with ethyl iodide (1.36 g, 0.01 mol) in ethanol (10 ml) and the reaction mixture is heated under reflux for 3 h. The solid obtained after concentration and cooling is crystallised from light petroleum ether (b.p. 60-80°C), to give 8d as pale yellow crystals; yield: 82% (Table).

4-Arylmethyl-2,6-dimethylpyridazin-3(2H)-thiones 9:
A mixture of 4-arylmethyl-2,6-dimethylpyridazin-3(2H)-one (0.01 mol) and phosphorus pentasulphide (0.015 mol) in xylene (30 ml) is heated under reflux for 10 h. The reaction mixture is filtered while hot and most of solvent removed. The solid formed after cooling crystallised from light petroleum ether (b.p. 60-80°C) to give 9; yield: 37-41% (Table).

4-Arylmethyl-3-(2-cyanethythio)-6-methylpyridazines 10:
A mixture of 5 (0.01 mol) and acrylonitrile (0.64 g, 0.012 mol) in ethanol (20 ml) is treated with few drops of 10% sodium hydroxide solution and the mixture heated under reflux for 12 h. The yellow solid formed after cooling is crystallised from benzene to give 10; yield: 77-82% (Table).

4-Arylmethyl-2-(2-cyanothio)-6-methylpyridazin-3(2H)-ones 12:
The reaction is carried out as described for 10. The products are crystallised from benzene to give 12 as colourless crystals; yield: 80-86% (Table).

4-Arylmethyl-3-mercapto-6-methylpyridazines 5 from 10:
A suspension of 10 (0.01 mol) in 20% aqueous sodium hydroxide solution (25 ml) is heated under reflux till complete dissolution of the solid occurred (~10 h). The clear solution is cooled and concentrated hydrochloric acid (~12 ml) is added till the mixture is just acidic. The yellow solids formed are crystallised from benzene to give 5; yield: 65%; identified by m.p. and m.m.p. and superimposable I.R. spectra with authentic samples.

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